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Supplemental Technical Development Document for Effluent Limitations Guidelines and Standards for the Pulp, Paper, and Paperboard Category

Subpart B (Bleached Papergrade Kraft and Soda) and Subpart E (Papergrade Sulfite)

SUPPLEMENTAL TECHNICAL DEVELOPMENT DOCUMENT FOR EFFLUENT LIMITATIONS GUIDELINES AND STANDARDS FOR THE PULP, PAPER, AND PAPERBOARD CATEGORY SUBPART B (BLEACHED PAPERGRADE KRAFT AND SODA)

SUBPART E (PAPERGRADE SULFITE)

AND

Engineering and Analysis Division Office of Science and Technology U.S. Environmental Protection Agency Washington, D.C. 20460

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SECTION 1

CONCLUSIONS

1.1 Introduction

The new regulations for the pulp, paper, and paperboard industry, also known as the "Cluster Rules," include effluent limitations guidelines and standards for the control of wastewater pollutants and national emission standards for hazardous air pollutants. Information and rationale supporting the proposed effluent limitations guidelines and standards were provided in "Proposed Technical Development Document for the Pulp, Paper, and Paperboard Category Effluent Limitations Guidelines, Pretreatment Standards, and New Source Performance Standards," (the TDD) October 1993, EPA-821-R-93-019. Technical information and rationale supporting the proposed air emission standards were provided in "Pulp, Paper, and Paperboard Industry - Background Information for Proposed Air Emission Standards," (the Background Information Document, or the BID) October 1993, EPA-453-R93-050a.

To support the final regulations, EPA chose not to rewrite the entire TDD and the BID but instead to prepare several technical support documents to supplement the TDD and the BID. This document, and several others referenced herein, support the final effluent limitations guidelines and standards. The TDD is superseded to the extent that this document or the other technical documents supporting the final rule are inconsistent with it. This document is referred to in the other support documents as the Supplemental Technical Development Document (STDD), Document Control Number (DCN) 14487. This section of the STDD highlights key aspects of the final effluent limitations guidelines and standards.

1.2 <u>Subcategorization</u>

EPA is revising the existing subcategorization scheme for effluent limitations guidelines and standards for this industry (40 CFR Parts 430 and 431). The new effluent limitations guidelines and standards that are being promulgated today affect only those mills in the new Bleached Papergrade Kraft and Soda Subcategory (Subpart B) and the new Papergrade Sulfite Subcategory (Subpart E). EPA has reprinted in their entirety the current effluent limitations guidelines and standards that remain applicable to mills subject to the new subcategories. Table 1-1 summarizes the new subcategories and the corresponding subcategories from the existing regulations.

1.3 Scope of Rules

The proposed rules applied to mills within the U.S. Department of Commerce, Bureau of the Census Standard Industrial Classifications (SIC) 2611 (pulp mills), 2621 (paper mills except building paper mills), 2631 (paperboard mills), and 2661 (building paper and building board mills). All of the mills affected by the new effluent limitations guidelines and standards are in SIC 2611 (pulp mills). Since the proposal, the Office of Management and

Budget began to use the North American Industry Classification System (NAICS). The applicable NAICS numbers are 32211 (pulp mills), 322121 (paper mills, except newsprint mills), 322122 (newsprint mills), and 32213 (paperboard mills). The components of these rules applicable to each subcategory of the Pulp, Paper, and Paperboard Point Source Category are shown on Table 1-2.

1.4 Best Practicable Control Technology Currently Available (BPT)

EPA proposed revisions to the existing BPT effluent limitations guidelines for five-day biochemical oxygen demand (BOD₅) and total suspended solids (TSS) for all subcategories of the pulp, paper, and paperboard industry. The proposed revisions were based on the application of secondary wastewater treatment with appropriate water use and reuse. However, for the reasons set forth in the preamble to the final rules, EPA in the exercise of its discretion has decided not to revise the BPT effluent limitations guidelines for conventional pollutants for Subparts B and E. The existing BPT guidelines will continue to apply.

1.5 <u>Best Conventional Pollutant Control Technology (BCT)</u>

EPA proposed revisions to the BCT effluent limitations guidelines for BOD₅ and TSS for all subcategories of the pulp, paper, and paperboard industry. After proposal, EPA considered further whether technologies are available for Subparts B and E that achieve greater removals of conventional pollutants than the current BPT effluent limitations guidelines, and whether those technologies are cost reasonable according to the BCT cost test. After evaluating the candidate BCT technologies for both Subparts B and E, EPA concluded that none of the candidate options passed the BCT cost test; therefore, more stringent BCT effluent limitations guidelines are not being promulgated for Subparts B or E.

1.6 Best Available Technology Economically Achievable (BAT)

EPA is promulgating BAT effluent limitations guidelines for Subparts B and E to control toxic and nonconventional pollutants in the bleach plant effluent and in the end-of-pipe effluent. For Subpart B mills, the technology basis for these effluent limitations guidelines is complete (100 percent) substitution of chlorine dioxide for chlorine in the bleaching process along with the other elements as presented in Section 8 of this document. For Subpart E mills, the technology basis for these effluent limitations guidelines is either complete (100 percent) substitution of chlorine dioxide for chlorine in the bleaching process and other elements, or totally chlorine-free (TCF) bleaching. Section 8 of this document explains these options in more detail.

In addition to the effluent limitations guidelines based on complete substitution, EPA is promulgating for Subpart B the Voluntary Advanced Technology Incentives Program for direct discharging mills that have or plan to install advanced technology beyond that which forms the basis of today's BAT and New Source Performance Standards (NSPS). The Incentives

Program is discussed in more detail in a separate document entitled "Technical Support Document for the Voluntary Advanced Technology Incentives Program, DCN 14488."

1.7 New Source Performance Standards (NSPS)

EPA is revising the NSPS for toxic, nonconventional, and conventional (BOD₅ and TSS) pollutants for Subpart B. For Subpart B mills, the technology basis for these limitations is extended delignification followed by complete (100 percent) substitution of chlorine dioxide for chlorine in the bleaching process, well-operated biological treatment, and other elements as presented in Section 8 of this document. For Subpart E mills, EPA is revising the NSPS for toxic and nonconventional pollutants. For Subpart E mills, the technology basis for these limitations is the same as the BAT limitations.

1.8 Pretreatment Standards for Existing Sources (PSES)

EPA is revising the PSES for toxic and nonconventional pollutants for Subparts B and E. The technology basis of these standards is the same as the basis for the BAT limitations promulgated today, with the exception of biological treatment. Mills must monitor for compliance with these standards at the bleach plant effluent.

1.9 Pretreatment Standards for New Sources (PSNS)

EPA is revising the PSNS for toxic and nonconventional pollutants for Subparts B and E. The technology basis of these standards is the same as the basis for the NSPS limitations promulgated today, with the exception of biological treatment. Mills must monitor for compliance with these standards at the bleach plant effluent.

1.10 <u>Best Management Practices (BMP)</u>

EPA is promulgating BMPs for direct and indirect discharging mills regulated under Subparts B and E. These BMPs are intended to prevent or otherwise contain leaks and spills and to control intentional diversions of spent pulping liquor, soap, and turpentine. The BMPs will reduce wastewater loadings of nonchlorinated toxic compounds and hazardous substances and, as an incidental matter, loadings of other pollutants. These BMPs are discussed in more detail in a separate document entitled "Technical Support Document for Best Management Practices for Spent Pulping Liquor Management, Spill Prevention, and Control, DCN 14489."

Comparison of the Final Codified Subcategorization Scheme

With the Previous Subcategorization Scheme

Table 1-1

New **Existing Subcategorization Scheme (With** Existing 40 CFR Part 430 Subparts Noted) **Subpart New Subcategorization Scheme** Dissolving Kraft Dissolving Kraft (F) В Bleached Papergrade Kraft and Soda Market Bleached Kraft (G), BCT Bleached Kraft (H), Fine Bleached Kraft (I), Soda (P) C Unbleached Kraft Unbleached Kraft (A) - Linerboard - Bag and Other Products Unbleached Kraft and Semi-Chemical (D, V) D Dissolving Sulfite Dissolving Sulfite (K) - Nitration - Viscose - Cellophane - Acetate E Papergrade Sulfite Papergrade Sulfite (J,U) - Blow Pit Wash - Drum Wash F Semi-Chemical Semi-Chemical (B) - Ammonia - Sodium G Mechanical Pulp GW-Thermo-Mechanical (M), GW-Coarse, Molded, News (N) GW-Fine Papers (O) GW-Chemi-Mechanical (L) Η Non-Wood Chemical Pulp Non-Wood Chemical Pulp Mills I Deink Secondary Fiber (Q) Secondary Fiber Deink - Fine Papers - Tissue Papers - Newsprint J Secondary Fiber Non-Deink Tissue from Wastepaper (T) Paperboard from Wastepaper (E) - Corrugating Medium - Non-Corrugating Medium Wastepaper-Molded Products (W) Builders' Paper and Roofing Felt (40 CFR Part 431 Subpart A)

Table 1-1 (Continued)

New Subpart	New Subcategorization Scheme	Existing Subcategorization Scheme (With Existing 40 CFR Part 430 Subparts Noted)
K	Fine and Lightweight Papers from Purchased Pulp	Non-Integrated Fine Papers (R) - Wood Fiber Furnish - Cotton Fiber Furnish Lightweight Papers (X) - Lightweight Papers - Lightweight Electrical Papers
L	Tissue, Filter, Non-Woven, and Paperboard from Purchased Pulp	Non-Integrated - Tissue Papers (S) - Filter and Non-Woven (Y) - Paperboard (Z)

See the <u>Code of Federal Regulations</u> (CFR), Title 40, Chapter I, volume including Parts 425 to 699, Part 430, edition as of July 1, 1997, for the subcategorization scheme being supercoded. See the CFR edition to be published as of July 1, 1998, for the final codified subcategorization scheme.

Table 1-2

Application of Rules to Pulp, Paper, and Paperboard Subcategories

			Clean Water Act			
New Effluent Guidelines Subcategory	New Effluent Guidelines Subpart	Clean Air Act NESHAP ^a	Toxic & Nonconventionalb: BAT, NSPS, PSES, and PSNS	Conven- tional ^c : NSPS	ВМР	
Dissolving Kraft	A	X				
Bleached Papergrade Kraft and Soda	В	X	X	X	X	
Unbleached Kraft	С	X				
Dissolving Sulfite	D	X				
Papergrade Sulfite	Е	X	X	X^d	X	
Semi-Chemical	F	X				
Mechanical Pulp	G	X ^e				
Non-Wood Chemical Pulp	Н	X ^e				
Secondary Fiber Deink	I	X ^e				
Secondary Fiber Non-Deink	J	X ^e				
Fine and Lightweight Papers from Purchased Pulp	K	X ^e				
Tissue, Filter, Non-Woven, and Paperboard from Purchased Pulp	L	Xe				

^aNational Emission Standards for Hazardous Air Pollutants.

^bToxic and nonconventional pollutants in this rulemaking include: 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), 2,3,7,8-tetrachlorodibenzofuran (TCDF), chloroform, 12 chlorinated phenolic compounds and adsorbable organic halides (AOX). The 12 chlorinated phenolic compounds include trichlorosyringol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 3,4,5-trichlorocatechol, 3,4,5-trichloroguaiacol, 3,4,6-trichlorocatechol, 3,4,6-trichloroguaiacol, 4,5,6-trichloroguaiacol, tetrachlorocatechol, tetrachloroguaiacol, 2,3,4,6-tetrachlorophenol, and pentachlorophenol. ^cConventional pollutants in this rulemaking include BOD₅ and TSS.

^dEPA is not promulgating NSPS for conventional pollutants for Subpart E. Existing standards continue to apply. ^eRule applies if these mills operate a bleach plant that uses chlorine or chlorine dioxide.

SECTION 2

SCOPE OF RULEMAKING

2.1 Introduction

Approximately 565 pulp, paper, and paperboard mills operate in the United States (1). Most of these mills are subject to effluent limitations guidelines or standards as a result of regulations promulgated in the 1970s and 1980s. These existing regulations are based on the division of the mills into 26 subcategories. Each subcategory is defined by processes employed and/or products manufactured, and has a separate set of effluent regulations.

In 1993, EPA proposed revisions to the existing effluent regulations for all 565 mills and new regulations for some mills. EPA also proposed to consolidate the existing 26 subcategories into 12 new subcategories, based primarily on the pulping process used at each mill. In today's rulemaking, EPA is promulgating the revised subcategorization scheme. However, at this time, EPA is not revising the existing effluent regulations for any mills except those mills in two of the revised subcategories: Bleached Papergrade Kraft and Soda mills (Subpart B) and Papergrade Sulfite mills (Subpart E). The number of mills in each of these subcategories is discussed in Section 4 of this document.

In 1993, EPA also proposed national emission standards for hazardous air pollutants (NESHAPs) for some of the 565 mills. EPA's proposed NESHAPs would affect pulp mills in six effluent guideline subcategories (see Tables 1-2 and 2-1). Although the industry was not originally subcategorized, EPA has subcategorized the industry since the proposal for the purposes of selecting the maximum achievable control technologies (MACT) which form the basis of the NESHAPs. EPA established four subcategories for mills that chemically pulp wood fiber: kraft, sulfite, soda, and semichemical. EPA's Office of Air and Radiation (OAR) also separated the MACT standards into three components: MACT I, MACT II, and MACT III. Each component of the MACT standards is described in Section 2.3.

2.2 Effluent Limitations Guidelines and Standards

The Clean Water Act (CWA) authorizes EPA to develop the regulations to control the amount of pollutants discharged to navigable waters of the United States by industrial dischargers. In 1993, for the Pulp, Paper, and Paperboard Point Source Category, EPA proposed the following regulations:

BPT (best practicable control technology currently available);

BCT (best conventional pollutant control technology);

BAT (best available technology economically achievable);

NSPS (new source performance standards);

PSES (pretreatment standards for existing sources); and

PSNS (pretreatment standards for new sources).

These regulations establish quantitative limits on the discharge of pollutants from industrial point sources. As explained in the preamble and in Section 12 of this document, EPA decided not to promulgate proposed regulations for BPT and BCT; however, previously promulgated BPT and BCT regulations remain in effect. Regulations for BAT, NSPS, PSES, and PSNS are being promulgated. The applicability of the various regulations is summarized below:

	Direct Discharge	Indirect Discharge	Existing Source	New Source	Conventional Pollutants	Toxic and Nonconventional Pollutants
BPT	X		X		X	
ВСТ	X		X		X	
BAT	X		X			X
NSPS	X			X	X	X
PSES		X	X			X
PSNS		X		X		X

All of these regulations are based upon the performance of specific technologies but do not require the use of any specific technology. The regulations applicable to direct dischargers are effluent limitations guidelines, applied to pretreatment individual facilities through National Pollutant Discharge Elimination System (NPDES) permits issued by EPA or authorized states under Section 402 of the CWA. The regulations applicable to indirect dischargers are pretreatment standards, administered by local permitting authorities (i.e., the government entity controlling the Publicly Owned Treatment Works (POTW) to which the industrial wastewater is discharged). The pretreatment standards are designed to control pollutants that pass through or interfere with POTWs.

EPA is now promulgating BAT, NSPS, PSES, and PSNS for two subcategories of the Pulp, Paper, and Paperboard Point Source Category: the Bleached Papergrade Kraft and Soda Subcategory (Subpart B) and the Papergrade Sulfite Subcategory (Subpart E). The Bleached Papergrade Kraft and Soda Subcategory is comprised of 86 mills that use a kraft or soda pulping process followed by a bleach plant (see Section 4). The Papergrade Sulfite Subcategory is comprised of 11 mills that use a sulfite pulping process; ten of the these mills have a bleach plant while one mill makes unbleached pulp.

In 1993, EPA had also proposed regulations requiring the implementation of BMPs. EPA is now promulgating BMP regulations applicable to direct and indirect discharging mills with pulp production in Subpart B or Subpart E.

2.3 NESHAPs

In 1990, Congress passed comprehensive amendments to Section 112 of the Clean Air Act. The objective of these amendments is to reduce nationwide air toxic emissions. Congress identified 189 "hazardous air pollutants" (HAPs) to be controlled by a regulatory structure based on source categories. NESHAPs based on Maximum Achievable Control Technology (MACT) must be established for new and existing sources. In no case can the NESHAPs be less stringent than the "MACT floor" for existing sources, which, roughly paraphrasing, requires the standard to be at least as stringent as the average emission limitation achieved by the best performing 12 percent of sources (Clean Air Act (CAA) Section 112(d)(2)). For more detailed discussion, see Section VI.A of the preamble for the final rules.

NESHAPs for the pulp and paper manufacturing source category are divided into three parts:

MACT I controls emissions from noncombustion sources from pulping and bleaching operations at chemical (kraft, soda, and sulfite) and semichemical wood pulping mills.

MACT II (which is being proposed) controls emissions from combustion sources (e.g., recovery furnaces, lime kilns, smelt dissolving tanks) from chemical recovery operations at wood pulping mills (kraft, soda, sulfite, and semichemical).

MACT III addresses emissions from noncombustion sources from mills that mechanically pulp wood, pulp secondary fibers, or pulp nonwood materials, and those that use papermachine additives and solvents.

MACT I controls primarily volatile HAPs, while MACT II controls metal HAPs.

For bleached papergrade kraft and soda mills, MACT I (for the most important emission points) is based on the performance of the following control technologies:

Collection and destruction of organic HAPs emitted by pulping area vents;

Controls on condensate streams from the digester system, evaporator system, turpentine recovery system, and high volume low concentration (HVLC) vents (brown stock washers and oxygen delignification (OD)), if any, but under a delayed compliance schedule (eight years) to encourage upgrade of brown stock washers and installation of OD;

Collection and treatment (caustic scrubber) of bleach plant vents to control hydrogen chloride and other chlorinated HAPs (other than chloroform);

Compliance with BAT limits on chloroform or elimination of hypochlorite and complete substitution of chlorine dioxide for elemental chlorine; and

Collection and treatment of pulping area condensates, including evaporator "foul" condensates by steam stripping or biological treatment.

For sulfite mills, MACT I is based on the performance of:

Collection and destruction of organic HAPs emitted by digester system vents, evaporator system vents, and pulp washing system vents;

Collection and neutralization (caustic scrubber) of organic HAPs emitted by bleach plant vents to control hydrogen chloride and other chlorinated HAPs (note that the scrubber does not control chloroform); and

Compliance with BAT limits on chloroform (these limits are based on elimination of hypochlorite and complete substitution of chlorine dioxide for elemental chlorine or totally chlorine free bleaching).

The MACT II proposal is based on:

Control of particulate HAPs by electrostatic precipitators (for recovery furnaces and lime kilns) and venturi scrubbers (for lime kilns and smelt dissolving tanks).

MACT I was proposed on December 17, 1993 (the same time as the effluent limitations guidelines) and is being promulgated today. MACT II is being proposed today. On September 29, 1995 a Presumptive MACT report was issued for the MACT III source category. Presumptive MACT is an estimate of MACT based on an assessment of readily available information and information gathered through consultation with experts in state and local agencies, EPA, environmental groups, and the regulated industry. No information was identified during the Presumptive MACT process to suggest that sources associated with the MACT III source category warrant listing pursuant to Section 112(c)(3) of the CAA.

Further, MACT III sources have no air pollution control devices, so the floor for these sources is no control. In addition, available information indicates add-on controls would not be cost effective for most emission points. EPA, therefore, decided in most instances not to require controls beyond the floor. Mills covered by MACT III must still collect and treat bleach

plant vents if they operate bleach plants that use chlorine or chlorinated compounds.

EPA has taken no action on MACT standards for chemical additives and solvents at the paper machines. If information becomes available regarding cost-effective HAP controls beyond the floor for these sources, EPA will propose a MACT standard in the future.

2.4 References

 Development Document for Proposed Effluent Limitations Guidelines and Standards for the Pulp, Paper, and Paperboard Point Source Category. EPA-821-R-93-019, U.S. EPA, Washington DC, October 1993.

Table 2-1

Application of Rules to Pulp, Paper, and Paperboard Subcategories

		Today's Clean Water Act Rules	Clean Air Act Rules			
NESHAP Subcategory	New Effluent Guidelines Subpart		MACT I	MACT II	MACT III	
Dissolving Kraft Pulping	A		X	X	X	
Papergrade Kraft and Soda Pulping	В	X	X	X	X	
Unbleached Kraft Pulping	С		X	X	X	
Dissolving Sulfite Pulping	D		X	X	X	
Papergrade Sulfite Pulping	E	X	X	X	X	
Semi-Chemical Pulping	F		X	X	X	
Mechanical Pulping	G				X^{a}	
Non-Wood Pulping	Н				X ^a	
Secondary Fiber Pulping	I, J				X ^a	
Papermaking Systems	K-L°				X^{b}	

^aIf these mills operate a bleach plant that uses chlorine or chlorine dioxide.

^bConsidered under MACT III but no controls are required.

^cApplicable to stand-alone papermaking systems; such systems at integrated mills are covered by the effluent limitations guidelines for the applicable subparts.

SECTION 3

SUMMARY OF DATA COLLECTION METHODS

3.1 Introduction

EPA collected information necessary for the development of the effluent limitations guidelines and standards from many sources, including several Agency and industry sampling programs, an industry-wide census questionnaire, questionnaire surveys submitted to mills in other countries, industry trade associations, public meetings, mill site visits, conferences, literature reviews, and other EPA offices. The data sources utilized for the proposed rules were described in the TDD. This section describes the data collected since proposal.

3.2 <u>Data Received Since Proposal</u>

EPA has gathered a substantial amount of new information and data since proposal. Much of this information was collected with the cooperation and support of the American Forest and Paper Association (AF&PA) and the National Council of the Paper Industry for Air and Stream Improvement Inc. (NCASI). Many individual mills in the U.S. and abroad, as well as environmental groups have also assisted in gathering this information. The comments received on the proposal and the July 1996 notice of data availability were also an important source of information. The data gathering activities for this final rule are summarized in detail in the proposal (58 <u>FR</u> at 66096), and in the July 15, 1996 notice of data availability (61 <u>FR</u> at 36837).

Some of the new information and data were generated through EPA-sponsored field sampling or visits at individual mills in the U.S., Canada, and Europe. Additional sampling data were voluntarily supplied by many facilities, along with information from laboratory and pilot-scale studies. In order to respond to and clarify comments on the proposal, the Agency also gathered and received voluntarily submitted information including data on secondary fiber mill processes, recovery furnace capacities, best management practices, capital and operating costs, process operations, and impacts of pollution prevention technology on the recovery cycle. Some of the major data collection activities are listed in Table 3-1 with references to the rulemaking record section(s) where the information can be found.

3.3 Integrated Regulatory Development

In 1990, EPA established the Pulp and Paper Regulatory Cluster, comprised of representatives from various EPA offices. One role of the Pulp and Paper Regulatory Cluster was to identify optimal approaches to solving environmental problems associated with the pulp and paper industry through regulatory coordination. As a result of the Cluster's efforts, the effluent limitations guidelines and the NESHAP rulemakings for the pulp and paper industry were integrated and jointly proposed. Regulation of land application of pulp and paper mill

sludge also was considered in the Agency's coordinated regulatory strategy. The joint proposal of the effluent limitations and NESHAPs eventually became known as the Cluster Rules.

The first step in developing the Cluster Rules was to collect mill-specific information from all facilities subject to both the effluent limitations and the NESHAPs. As described in Section 3.0 of the TDD, EPA used information from many sources to develop the integrated regulatory options proposed in 1993. The information collected includes the process and control technologies in use, data representing the performance of these technologies, and financial information used in the analysis of the economic impact of these options. This information was compiled in a mill-specific database for use in developing the effluent limitations and NESHAPs. Estimated costs, pollutant reductions, and other environmental impacts for each regulatory alternative were then developed and various combinations of these alternatives were analyzed. See the Economic Analysis (DCN 14649) for a detailed presentation of the economic and related analyses (3).

The control technologies considered as the bases for BAT, PSES, NSPS, and PSNS are described in Sections 7.0 and 8.0. The control technologies considered as the bases for BMP and NESHAP are described in separate documents (1,2). The control options for BAT and PSES involve pulping and bleaching process changes. The performance of existing secondary biological wastewater treatment systems employed by direct dischargers and POTWs also were considered in developing these options. The BMP requires prevention and control of leaks, spills, and intentional diversions of spent pulping liquor, soap, and turpentine. The NESHAP control technologies include steam strippers, combustion, and caustic scrubbing. Steam strippers are used to remove HAPs from pulping area condensates. The "clean condensate alternative" in the MACT I standards also allow mills as a compliance alternative to treat hard pipe condensates in end-of-pipe secondary biological treatment systems. See the preamble for the final rules at Section VI.A.3(d). Combustion devices are used to destroy non-chlorinated HAPs removed by steam strippers and hard-piped air emission streams. Combustion devices include stand-alone devices such as thermal incinerators or existing devices such as lime kilns, power boilers, and recovery furnaces. Caustic scrubbers and process changes are used to reduce chlorinated HAP emissions in the bleaching area.

EPA developed regulatory alternatives based on pulping and bleaching process changes alone, air emission control options alone, and combinations of process changes and air emission controls. Each regulatory alternative also included secondary wastewater treatment, and spill prevention and control components. The alternatives were designed to evaluate the most efficient application of control technologies to minimize the cross-media transfer of pollutants between air and water, and partitioning of pollutants (e.g., dioxins) to sludges and pulps. EPA's economic analysis summarizes the costs and benefits of each regulatory alternative evaluated by EPA for the final cluster rules (3).

EPA evaluated whether the pulping and bleaching process changes that form the basis of BAT and PSES reduce HAP emissions sufficiently to satisfy CAA requirements. Based on available data, the analyses showed that the use of the bleaching process technologies

decrease uncontrolled emissions of chlorinated HAPs (including chloroform, chlorine, and hydrochloric acid), but increase others. This decrease in uncontrolled air emissions of chlorinated HAPs is attributable to the elimination of hypochlorite as a bleaching agent and use of complete chlorine dioxide substitution. However, uncontrolled air emissions of some non-chlorinated HAPs, including methanol, methyl ethyl ketone, and formaldehyde, show modest increases as a result of the bleaching process changes (see Section 11). EPA decided that the bleaching process changes and existing bleach plant caustic scrubbers sufficiently reduced and controlled emissions of chlorinated HAPs. However, additional controls were needed in the pulping area to satisfy the CAA requirements for non-chlorinated HAPs.

EPA also considered the effect of the air pollution controls on effluent loadings of toxic and nonconventional pollutants. The analyses showed that the major air pollution controls that form the basis for NESHAP (steam stripping, combustion, and caustic scrubbing) did not significantly affect effluent loadings of these pollutants. Steam stripping systems remove compounds from pulping area condensates. Combustion destroys the compounds removed from the condensates along with most compounds emitted from process vents. Steam stripping and combustion reduce the amount of pollutants that could enter surface waters due to deposition and the volume of wastewater discharged to the wastewater treatment system. Chlorinated HAPs that remain in bleaching area wastewaters after process changes are implemented react with caustic in the scrubber, neutralizing the caustic effluent. Non-chlorinated HAPs that absorb into the caustic are bio-degradable, and are not estimated to significantly increase the pollutant load to the wastewater treatment system. Caustic scrubbing operations are also not expected to significantly increase the volume of wastewater discharges to the wastewater treatment system.

The analyses of multiple regulatory alternatives showed that no single control or process change technology is currently available to reduce pollutant discharges to the air and water to levels required by the respective statutes. The demonstrated control technologies that can serve as bases for BMP, BAT, PSES, NSPS, and PSNS pose no significant adverse impacts to and have some benefits for air quality. Similarly, the BMPs reduce leaks and spills and are capable of reducing intentional diversions of pulping liquors, soaps, and turpentine while increasing recovery of important process chemicals and energy (1); the air emissions control technologies that can serve as the basis for NESHAP pose no significant adverse impacts on and have some benefits for water quality. Therefore, combining the best control technology options for effluent limitations with the best control technology options for air emission standards represents a reasonable method for constructing the final regulatory alternative. EPA selected control options for the final rulemaking based on evaluation of pollutant reductions; costs; and economic, nonwater quality and non-air quality, and energy impacts (3). EPA also considered cost effectiveness and environmental impacts.

3.4 <u>References</u>

- Technical Support Document for Best Management Practices for Spent Pulping Liquor Management, Spill Prevention, and Control. EPA, Washington DC, Record Section 30.9, DCN 14489, 1997.
- 2. Anderson, Donald F., Memorandum on Data Available for Development of COD Limitations. Record Section 22.4, DCN 14788, September 30, 1997.
- 3. Economic Analysis for the National Emission Standards for Hazardous Air

 Pollutants for Source Category: Pulp and Paper Production; Effluent Limitations
 Guidelines, Pretreatment Standards, and New Source Performance Standards:
 Pulp, Paper, and Paperboard Category Phase I. Prepared by ERG for EPA.
 Record Section 30.5, DCN 14649, 1997.

Table 3-1

Major Post-Proposal Data Sources

Data Source	Record Section	
Public Comments	19.1	
Voluntary Data Submissions from Industry (NCASI, AF&PA) Secondary Fiber Questionnaires Recovery Furnace Capacity Surveys BMP Questionnaire Capital and Operating Cost Requests Operating Data Requests for Recently Installed Pulping and Bleaching Technologies Request for Information About the Impact of Technologies on the Recovery Cycle	21.1 21.1.1 21.1.2 21.1.3 21.1.4 21.1.5	
Data Supplied by Individual U.S. Mills	21.6.1.1	
Data Collected by EPA at U.S., Canadian, and European Mills	21.6.1.2	
Data Supplied by NCASI from Canadian Mills	21.6.1.7	
Laboratory Trial Data Submitted by Individual Companies (Dissolving Mills and Papergrade Sulfite Mills)	21.11	
Other Data Supplied by NCASI	21.12	

SECTION 4

INDUSTRY PROFILE

4.1 Introduction

This section discusses the number of pulp and paper mills included in the effluent limitations guidelines analyses. The mill counts in this section have been updated for the Bleached Papergrade Kraft and Soda and Papergrade Sulfite subcategories only.

The Office of Water promulgation baseline is mid-1995. The EPA mid-1995 database includes 86 bleached papergrade kraft and soda mills and 11 papergrade sulfite mills. The total number of bleached kraft mills was reduced from 88 at proposal to 86 now, due to the closing of one bleached papergrade kraft mill (Simpson Paper, Fairhaven, CA) and the reclassification of another mill as unbleached kraft (Port Townsend, Port Townsend, WA). All 11 papergrade sulfite mills (one mill received BMP cost estimates only, Great Northern Paper, Millinocket, ME) and 84 of the 86 bleached papergrade kraft and soda mills have been included in EPA's mid-1995 cost and loading estimation efforts (See Section 10 and Section 9, respectively). Note that one mill manufactures both bleached papergrade kraft and papergrade sulfite pulp, so there are a total of 96 mills in the two subcategories.

Table 4-1 lists the mills not included in the costs and loadings analyses presented in the July 1986 notice. Costs and loadings estimates for the Georgia-Pacific specialty grade sulfite mill in Bellingham, WA were not included in the July 1996 Notice. Estimates for this mill are included, however, in the results presented in this document. As of mid-1995, the Bellingham mill was the only mill in the Specialty Grade segment of Subpart E. EPA expects another papergrade sulfite facility to enter the specialty-grade market in the near future. Also, Badger Paper's papergrade sulfite mill in Peshtigo, WI shut down its pulping process in September 1996 (paper making operations have continued) but is *still included* in the analyses because EPA's baseline remained mid-1995.

Table 4-2 provides a summary of applicability and mill counts by subcategory. The table shows each component of the joint rulemaking (MACT, BAT, PSES, and BMPs) and illustrates that **all** components apply to mills in the bleached papergrade kraft and soda and papergrade sulfite subcategories. Because EPA decided not to revise BPT and BCT, these regulations have been removed from this analysis. Table 4-3 shows the applicability of each component for each of the 97 mills currently included in EPA's database.

Additional details on applicability for each of the effluent guideline subcategories included in the rulemaking are presented in the following subsections.

4.2 Bleached Papergrade Kraft and Soda Subcategory

The bleached papergrade kraft and soda mills subject to BAT, PSES, MACT, and BMPs as well as specific mills that did not receive costs or loadings estimates are discussed below.

Of the 86 bleached papergrade kraft and soda mills, **84** mills produce bleached papergrade kraft products and **2** produce bleached papergrade soda products.

MACT applies to these **86** mills.

One mill (James River, Camas, WA) produces both bleached papergrade kraft and bleached papergrade sulfite products (and is counted in both subcategories).

One mill (Stone Container Corp., Snowflake, AZ) did not receive costs and loadings estimates even though BAT/PSES and BMPs apply. The mill has announced it will cease bleached kraft production. The mill currently has a functional bleach plant and is counted in the bleached kraft subcategory, but is expected to be reclassified as unbleached kraft after promulgation. Costs and loadings will be estimated in the phase II rulemaking for unbleached kraft production.

One mill (Port Townsend Paper, Port Townsend, WA) does not have a conventional bleach plant, and only brightens with peroxide and sodium hydroxide. This mill was counted as bleached papergrade kraft at proposal but has now been reclassified as unbleached kraft.

One mill (Longview Fibre, Longview, WA) shut down its chlorine-based bleach plant in March 1994. In 1995 and through October 1996, a small amount of semi-bleached pulp using one stage of peroxide bleaching was processed. EPA did not estimate compliance costs and loadings reductions for this mill. But, because the mill has a functional bleach plant, it has not been reclassified as unbleached kraft. BAT/PSES and BMPs apply but no costs or loadings were estimated, on the assumption that the mill would cease bleached kraft production rather than invest in new bleaching technology. Costs and loadings will be estimated in the phase II rulemaking for unbleached kraft production.

Of the 77 mills to which BAT applies, **75** received BAT cost and loading estimates. (As mentioned previously, cost and loading estimates were not prepared for Stone Container, Snowflake, and Longview Fibre, Longview.)

PSES applies to 9 mills.

BMPs apply to **86** mills. BMPs apply to Stone Container, Snowflake and Longview Fibre, Longview, but no BMP costs were estimated, based on the assumption they have or will cease bleached kraft production.

4.3 <u>Papergrade Sulfite Subcategory</u>

The papergrade sulfite mills subject to BAT, PSES, MACT, and BMPs along with the one mill that only received BMP costs are described below.

In the U.S., 11 mills currently produce papergrade sulfite products (the papergrade sulfite subcategory covers mills with both bleached and unbleached production).

One mill produces only unbleached sulfite products. BAT applies, but they are assumed to have no cost. BMP costs were estimated.

One mill (James River, Camas, WA) produces both bleached papergrade kraft and bleached papergrade sulfite products (and is counted in both subcategories).

One of the mills is both a direct and an indirect discharger. However, wastewater from its pulping and bleaching operations is discharged to a POTW, so this mill is covered by PSES for the papergrade sulfite subcategory, not BAT.

MACT applies to 11 mills.

Of the 10 mills to which BAT applies, **9** received cost and loadings estimates.

PSES applies to 1 mill.

BMPs apply to 11 mills.

4.4 Trends in the Industry

The development of increasingly more advanced process technologies that minimize the discharge of wastewater and wastewater pollutants is a critical step toward the Clean Water Act's ultimate goal of eliminating the discharge of pollutants into the nation's waters. EPA is interested in encouraging development of advanced technologies for broader commercial applications (1). As these technologies become proven and their efficiencies publicized, EPA hopes that they will become standard industry practice. Thus, EPA believes it is

in the public interest to encourage mills today to develop environmentally beneficial technology and to provide incentives for mills that are innovative and forward-looking in their use of new technologies that are more environmentally and cost effective despite their greater initial capital cost.

4.5 <u>References</u>

1. <u>Technical Support Document for the Voluntary Advanced Technology Incentives</u>
<u>Program.</u> EPA, Washington DC, Record Section 22.8, DCN 14488.

Table 4-1
Mills Omitted from EPA's Mid-1995 BAT/PSES Cost and Loadings Estimates

Subcat.	Company	Location	Reason for Omission
В	Stone Container Corp.	Snowflake, AZ	Mill is expected to cease bleached pulp production before Cluster Rules take effect. Removed from costs and loadings estimates.
В	Simpson Paper Co.	Fairhaven, CA	Closed in March 1993
Е	Great Northern Paper	Millinocket, ME	Unbleached sulfite (BMP costs only)
С	Port Townsend Paper	Port Townsend, WA	No bleach plant but was misclassified as BPK at proposal
В	Longview Fibre Co.	Longview, WA	Chlorine-based bleaching curtailed March 1994

Table 4-2
Mid-1995 Applicability and Mill Counts by Subcategory

	Number of	Clean Air	Clean Water Act					
Effluent Subcategory	Mills in this Subcategory	Act MACT	BAT	PSES	BMP			
Bleached Papergrade Kraft and Soda	86	86	77	9	86			
Papergrade Sulfite	11	11	10	1	11			
Number of Mills Affected ^a	96	96	86	10	96			

^aOne mill has production in both subcategories so total mills affected is one less than the sum of the mills in the two subcategories.

Table 4-3

Applicability by mill for the Bleached Papergrade Kraft and Soda and Papergrade Sulfite Facilities

Company	Mill	State	Subcat	Discharge Status	MACT	ВАТ	PSES	ВМР	Comments
Alabama Pine Pulp	Claiborne (Perdue Hill)	AL	В	Direct	``	`	1525	``	
Alabama River Pulp Co. Inc.	Claiborne (Perdue Hill)	AL	В	Direct	`	`		`	
Appleton Papers Inc.	Roaring Spring	PA	В	Direct	`	`		`	
Badger Paper Mills Inc.	Peshtigo	WI	Е	Direct, Indirect	,		`	`	Recently shut down its pulping process.
Boise Cascade Corp.	Deridder	LA	В	Direct	`	`		`	
Boise Cascade Corp.	International Falls	MN	В	Direct	`	`		`	
Boise Cascade Corp.	Jackson	AL	В	Direct	`	`		`	
Boise Cascade Corp.	St. Helens	OR	В	Indirect	`		`	`	
Boise Cascade Corp.	Wallula	WA	В	Direct	`	`		`	
Bowater Inc.	Calhoun	TN	В	Direct	`	`		`	
Bowater Inc.	Catawba	SC	В	Direct	`	`		`	
Champion International Corp.	Canton	NC	В	Direct	`	`		`	
Champion International Corp.	Cantonment (Pensacola)	FL	В	Direct	`	`		`	
Champion International Corp.	Courtland	AL	В	Direct	`	`		`	
Champion International Corp.	Houston (Sheldon)	TX	В	Direct	`	`		`	
Champion International Corp.	Lufkin	TX	В	Direct	`	`		`	
Champion International Corp.	Quinnesec (Norway)	MI	В	Direct	`	`		`	
Chesapeake Paper Products Co.	West Point	VA	В	Direct	`	`		`	
Consolidated Papers Co.	Wisconsin Rapids	WI	В	Direct	`	`		`	
Container Corp. of America (Jefferson Smurfit)	Brewton	AL	В	Direct	`	`		`	

				Discharge					
Company	Mill	State	Subcat	Status	MACT	BAT	PSES	BMP	Comments
Federal Paper Board Co. (International Paper)	Augusta	GA	В	Direct	`	`		`	
Federal Paper Board Co. (International Paper)	Riegelwood	NC	В	Direct	`	`		`	
Finch Pruyn & Co Inc.	Glens Falls	NY	Е	Direct	`	`		`	
Fraser Paper (Cross Pointe)	Park Falls	WI	Е	Direct	`	`		`	
Georgia-Pacific Corp.	Ashdown	AR	В	Direct	`	`		`	
Georgia-Pacific Corp.	Bellingham	WA	Е	Direct	`	`		`	
Georgia-Pacific Corp.	Brunswick	GA	В	Direct	`	`		`	
Georgia-Pacific Corp.	Crossett	AR	В	Direct	`	`		`	
Georgia-Pacific Corp. (Nekoosa)	Nekoosa	WI	В	Direct	`	`		`	
Georgia-Pacific Corp. (Leaf River)	New Augusta	MS	В	Direct	`	`		`	
Georgia-Pacific Corp.	Palatka	FL	В	Direct	`	`		`	
Georgia-Pacific Corp. (Nekoosa)	Port Edwards	WI	Е	Direct	`	`		`	
Georgia-Pacific Corp.	Woodland	ME	В	Direct	`	`		`	
Georgia-Pacific Corp.	Zachary (Port Hudson)	LA	В	Direct	`	`		`	
Gilman Paper Co.	St. Marys	GA	В	Direct	`	`		`	
Great Northern Paper Co.	Millinocket	ME	E	Direct	`	`		`	Only unbleached sulfite.
Gulf States Paper Corp.	Demopolis	AL	В	Direct	`	`		`	
International Paper Co.	Bastrop	LA	В	Direct	`	`		`	
International Paper Co.	Erie	PA	В	Indirect	`		`	`	
International Paper Co.	Georgetown	SC	В	Direct	`	`		`	
International Paper Co. (And'scogn)	Jay	ME	В	Direct	`	`		`	
International Paper Co.	Mobile	AL	В	Direct	`	`		`	
International Paper Co.	Moss Point	MS	В	Indirect	`		` `	`	

				Discharge					
Company	Mill	State	Subcat	Status	MACT	BAT	PSES	BMP	Comments
International Paper Co.(Hammermill)	Pine Bluff	AR	В	Direct	`	`		`	
International Paper Co. (Riverdale)	Selma	AL	В	Direct	`	`		`	
International Paper Co.	Texarkana	TX	В	Direct	`	`		`	
International Paper Co.	Ticonderoga	NY	В	Direct	`	`		`	
James River Corp. (Crown Paper Co.)	Berlin	NH	В	Direct	`	,		,	
James River II Inc	Camas	WA	Е	Direct	`	,		,	
James River II Inc	Camas	WA	В	Direct	`	`		`	
James River Corp. (Wauna Mill)	Clatskanie	OR	В	Direct	`	`		,	
James River Corp.	Old Town	ME	В	Direct	`	,		,	
James River Corp. (Naheola Mill)	Pennington	AL	В	Direct	`	`		`	
James River II Inc. (Crown Paper)	St. Francisville	LA	В	Direct	`	`		`	
Kimberly Clark Corp.	Coosa Pines	AL	В	Direct	`	`		`	
Kimberly-Clark Corp.	Everett	WA	Е	Direct	`	`		`	
Lincoln Pulp & Paper Co.	Lincoln	ME	В	Direct	`	`		`	
Longview Fibre	Longview	WA	В	Direct	`	,		,	No costs estimated.
Louisiana-Pacific Corp.	Samoa	CA	В	Direct	`	,		,	TCF bleaching process.
Mead Corp.	Chillicothe	ОН	В	Direct	`	`		`	
Mead Corp.	Escanaba	MI	В	Direct	`	`		`	
Mead Corp.	Rumford	ME	В	Direct	`	`		`	
P. H. Glatfelter Co.	Spring Grove	PA	В	Direct	`	`		`	
Pope & Talbot Inc.	Halsey	OR	В	Direct	`	`		`	

				Discharge					
Company	Mill	State	Subcat	Status	MACT	BAT	PSES	BMP	Comments
Port Townsend Paper	Port Townsend	WA	В	Direct					No bleach plant/Reclassified as unbleached kraft.
Potlatch Corp.	Cloquet	MN	В	Indirect	`		`	`	
Potlatch Corp.	Lewiston	ID	В	Direct	`	`		`	
Potlatch Corp.	McGehee	AR	В	Direct	`	`		`	
Procter & Gamble Paper	Mehoopany	PA	Е	Direct	`	`		`	
S.D. Warren (SAPPI)	Hinckley (Skowhegan)	ME	В	Direct	`	`		`	
S.D. Warren (SAPPI)	Muskegon	MI	В	Indirect	`		`	`	
S.D. Warren (SAPPI)	Westbrook	ME	В	Direct	`	`		`	
Scott Paper Co./SAPPI	Mobile	AL	В	Direct	`	`		`	
Simpson Paper Co.	Anderson	CA	В	Direct	`	`		`	
Simpson Paper Co.	Fairhaven	CA	В	Direct					Closed in March 1993.
Simpson Paper Co.	Pasadena	TX	В	Indirect	`		`	`	
Simpson Tacoma Kraft Co.	Tacoma	WA	В	Direct	`	`		`	
St. Joe Forest Products Co.	Port St. Joe	FL	В	Indirect	`		`	`	
Stone Container Corp.	Missoula	MT	В	Direct	`	`		`	
Stone Container Corp.	Panama City	FL	В	Indirect	`		`	`	
Stone Container (Savannah River)	Pt. Wentworth	GA	В	Direct	`	`		`	
Stone Container Corp.	Snowflake	AZ	В	N	`	`		`	No costs and loadings estimated.
Temple Inland Forest Products	Evadale (Silsbee)	TX	В	Direct	`	`		`	
Union Camp Corp.	Eastover	SC	В	Direct	`	`		`	

Company	Mill	State	Subcat	Discharge Status	MACT	BAT	PSES	ВМР	Comments
Union Camp Corp.	Franklin	VA	В	Direct	,	,		,	One OZ-ECF SWD line.
Wausau Paper Mills Co.	Brokaw	WI	Е	Direct	`	`		`	
Westvaco Corp.	Covington	VA	В	Direct	`	`		`	
Westvaco Corp.	Luke	MD	В	Indirect	`		`	`	
Westvaco Corp.	Wickliffe	KY	В	Direct	,	,		,	
Weyerhaeuser Paper Co.	Columbus	MS	В	Direct	`	`		`	
Weyerhaeuser Paper Co.	Longview	WA	В	Direct	,	,		,	
Weyerhaeuser Paper Co.	New Bern	NC	В	Direct	`	`		`	
Weyerhaeuser/Flint River Mill	Oglethorpe	GA	В	Direct	`	`		`	
Weyerhaeuser Paper Co.	Plymouth	NC	В	Direct	`	`		`	
Weyerhaeuser Paper Co.	Rothschild	WI	Е	Direct	,	,		,	
Willamette Industries Inc.	Bennetsville	SC	В	Direct	`	`		`	
Willamette Industries Inc.	Hawesville	KY	В	Direct	`	`		`	
Willamette (Penntech Papers Div.)	Johnsonburg	PA	В	Direct	,	`		`	
Willamette Industries Inc.	Kingsport	TN	В	Direct	`	`		`	

NA - Not Applicable, no costs and loadings were determined for this mill.

Note: James River, Camas, WA has production in both subcategories.

SECTION 5

SUBCATEGORIZATION

5.1 Introduction

EPA proposed a new subcategorization scheme to replace the former subcategorization scheme found in 40 CFR Part 430 (Pulp, Paper, and Paperboard Point Source Category) and 40 CFR Part 431 (The Builder's Paper and Board Mills Point Source Category). The new subcategorization scheme consolidates into 12 subcategories what had once been 26 subcategories. EPA's reasons for combining and reorganizing the subcategories are described in the proposal (see 58 FR 66098-66100) and in a document entitled "Selected Issues Concerning Subcategorization" (1). EPA solicited comment on whether any specific subcategories proposed should be divided into smaller subcategories and whether any specific subcategories proposed should be combined to form larger subcategories. This section provides a description of the industry subcategorization in effect prior to the promulgation of this rule, describes EPA's methodology in developing the proposed subcategorization scheme, provides summaries of comments received on the proposed subcategorization scheme, provides EPA's assessment of the subcategorization comments, and presents EPA's final determinations on the subcategorization scheme.

5.2 <u>Description of the Industry Subcategorization in Effect Prior to the</u> Promulgation of this Rule

Manufacturing processes and untreated wastewater characteristics (i.e., pollutant loadings which varied somewhat by final product produced) were the principal factors used to subcategorize the industry prior to this rulemaking. Data used to determine that subcategorization represented the state of the industry during the early-to-mid 1970s. At that time, the overall level of wastewater treatment provided by the industry was not consistent among mills with similar manufacturing processes. EPA concluded at that time that untreated wastewater pollutant loadings provided a reasonable basis to subcategorize the industry principally because the costs of compliance for mills with similar untreated wastewater pollutants loadings to achieve uniform effluent levels were similar.

The subcategorization in effect prior to the promulgation of this rule was:

40 CFR Part 430

- Subpart A Unbleached Kraft;
- Subpart B Semi-Chemical;
- Subpart C Reserved;
- Subpart D Unbleached Kraft-Neutral Sulfite Semi-Chemical (Cross Recovery);
- Subpart E Paperboard from Wastepaper;

- Subpart F Dissolving Kraft;
- Subpart G Market Bleached Kraft;
- Subpart H Board, Coarse, and Tissue (BCT) Bleached Kraft;
- Subpart I Fine Bleached Kraft;
- Subpart J Papergrade Sulfite (Blow Pit Wash);
- Subpart K Dissolving Sulfite Pulp;
- Subpart L Groundwood-Chemi-Mechanical;
- Subpart M Groundwood-Thermo-Mechanical;
- Subpart N Groundwood-Coarse, Molded, and News (CMN) Papers;
- Subpart O Groundwood-Fine Papers;
- Subpart P Soda;
- Subpart Q Deink Secondary Fiber;
- Subpart R Non-Integrated-Fine Papers;
- Subpart S Non-Integrated-Tissue Papers;
- Subpart T Tissue from Wastepaper;
- Subpart U Papergrade Sulfite (Drum Wash);
- Subpart V Unbleached Kraft and Semi-Chemical;
- Subpart W Wastepaper-Molded Products;
- Subpart X Non-Integrated-Lightweight Papers;
- Subpart Y Non-Integrated-Filter and Non-Woven Papers;
- Subpart Z Non-Integrated-Paperboard; and

40 CFR Part 431

Subpart A - Builders' Paper and Roofing Felt.

5.3 Revised Industry Subcategorization

Since the early-to-mid 1970s, all but one of the direct discharging mills have installed secondary wastewater treatment systems. End-of-pipe discharge data supplied in the 1990 Census Questionnaire for most mills show that the degree of end-of-pipe wastewater treatment provided by the industry is much more uniform than it was during the 1970s. In consideration of the factors in CWA Section 304(b), EPA has determined that the subcategorization analysis for this pulp, paper, and paperboard industry is more appropriately conducted based on manufacturing processes employed and engineering aspects of the application of various types of control techniques rather than raw waste loads. EPA believes that these factors more accurately represent a mill's ability to comply with effluent limitations guidelines and standards and achieve pollutant reductions.

As discussed in Section 5.3.1 of the Proposed Technical Development Document, the pulp, paper, and paperboard industry can be classified by major production processes. These production processes and the applicable former subcategories are listed below.

Integrated Pulp and Paper Mills

Chemical Pulp Mills

- Kraft and Soda Mills
 - Dissolving Kraft (Subpart F)
 - Bleached Papergrade Kraft (Subparts G, H, I)
 - Bleached Papergrade Soda (Subpart P)
 - Unbleached Kraft (Subparts A, D, V)
- Sulfite Mills
 - Dissolving Sulfite (Subpart K)
 - Papergrade Sulfite (Subparts J and U)
- Non-Wood Fiber Pulp Mills

Semi-Chemical Pulp Mills (Subparts B, D, V)

Mechanical Pulp Mills

- Stone Groundwood (Subparts N and O)
- ` Refiner
- ` Thermo-Mechanical (Subpart M)
- ` Chemi-Mechanical (Subpart L)
- ` Chemi-Thermo-Mechanical

Secondary Fiber Mills

- Deink Mills (Subpart Q)
- Non-Deink Mills (Subparts E, T, W, and Part 431 Subpart A)

Non-Integrated Paper Mills (Subparts R, S, X, Y, Z) (producers of products from purchased pulp)

The classification of the industry by major production processes addresses many of the statutory factors set forth in CWA Section 304(b), including manufacturing processes and equipment (e.g., chemical, mechanical, and secondary fiber pulping; pulp bleaching; paper making); raw materials (e.g., wood, secondary fiber, non-wood fiber, purchased pulp); products manufactured (e.g., unbleached pulp, bleached pulp, finished paper products); and, to a large extent, untreated and treated wastewater characteristics (e.g., BOD₅ loadings, presence of toxic chlorinated compounds from pulp bleaching) and process water usage and discharge rates. EPA determined that other factors such as size, age, and geographical locations were not significant factors to explain the technical feasibility or economic achievability of effluent limitations guidelines and standards for this industry. As a result, the Agency used the production process classifications described above as a starting point for reviewing subcategorization.

Most manufacturing processes at pulp, paper, and paperboard mills generate wastewaters that contain substantial quantities of the conventional pollutants BOD₅ and TSS.

Furthermore, efficient BOD₅ removal is a principal design objective for pulp, paper, and paperboard mill wastewater treatment systems. For these reasons, BOD₅ and TSS are important measures of pollution generation and wastewater treatability for the pulp and paper industry. Although EPA is making no changes to BPT and BCT conventional pollutant limitations previously promulgated for any subcategories at this time, EPA is revising NSPS for the conventional pollutants BOD₅ and TSS for the Bleached Papergrade Kraft and Soda Subcategory. In addition, effective secondary biological treatment is a component of the revised BAT and PSES technology bases for the Bleached Papergrade Kraft and Soda and the Papergrade Sulfite Subcategories. Therefore, EPA has determined that BOD₅ loadings are an important component of the Agency's subcategorization analysis.

EPA examined the status of the industry with respect to treatment of BOD_5 to determine if the former subcategories adequately represent current industry characteristics. The Agency determined that, based upon the present status of the industry, many of the former subcategories are no longer necessary because mills with similar production processes have, at reasonable costs, achieved similar production normalized effluent quality, notwithstanding differences in untreated wastewater pollutant loadings. Accordingly, EPA used effluent quality, in terms of final effluent production normalized BOD_5 load, as a basis to further subcategorize the industry beyond the major process classifications set forth above.

Using the methodology described in Section 5.0 of the Technical Development Document for the proposed rule (2), the Agency compared average and range of production-normalized final effluent BOD₅ loadings of the mills selected to represent each former subcategory. Subcategories with similar process technologies were compared. Based upon these comparisons, the Agency determined that several former subcategories exhibited similar treated wastewater characteristics, and that these subcategories might be grouped or combined into revised subcategories. EPA's revised subcategorization scheme is listed below (see also Table 1-1).

40 CFR Part 430

- Subpart A Dissolving Kraft;
- Subpart B Bleached Papergrade Kraft and Soda;
- Subpart C Unbleached Kraft;
- Subpart D Dissolving Sulfite;
- Subpart E Papergrade Sulfite;
- Subpart F Semi-Chemical;
- Subpart G Mechanical Pulp;
- Subpart H Non-Wood Chemical Pulp;
- Subpart I Secondary Fiber Deink;
- Subpart J Secondary Fiber Non-Deink;
- Subpart K Fine and Lightweight Papers from Purchased Pulp;
- Subpart L Tissue, Filter, Non-Woven, and Paperboard from Purchased Pulp.

5.3.1 All Mills

Some commenters on the proposed rule indicated that EPA should retain the former subcategorization scheme, which was based on an evaluation of raw waste loads and flows. One commenter stated that if EPA insists on revising the subcategories, the Agency must also evaluate raw waste loads, product type, fiber furnish, and raw waste treatability in addition to effluent loads.

EPA has determined that the groupings in Subparts A through L (excluding Subparts B and E discussed in Sections 5.3.2 and 5.3.3, respectively) are appropriate since they are comprised of mills using similar processes and attaining similar effluent quality. EPA will consider evaluating the relationship between raw waste loads and treated effluent waste loads along with other factors suggested by commenters that may affect the reasonableness of the groupings when EPA determines whether new or revised effluent limitations guidelines and standards are appropriate for these subcategories. At that time, EPA would likely consider in addition to other factors identified in CWA Section 304(b):

- Specific processes, including papermaking processes;
- ` Products:
- ` Fiber furnish:
- ` Grade changes;
- ` Chemical usage;
- Non-fibrous material (fillers, additives, coatings, etc.);
- ` Shrinkage;
- ` Raw material (fiber) quality;
- Product quality/requirements;
- Water requirements;
- Pollutant loadings; and
- ` Effluent quality.

If after further analysis EPA determines that certain types of mills within a subcategory cannot achieve the same effluent quality without undue economic impact, EPA will consider further segmenting the subcategory as appropriate to better respond to material differences between facilities. In the interim, the subcategorization scheme for these subcategories is simply a redesignation of the old subcategories into the new subcategories. The limitations and standards promulgated under the old subcategorization scheme are recodified under the new subcategorization scheme in the form of segments corresponding to the old subparts. (In recodifying these limitations and standards, EPA has not changed the substance of the existing regulations.)

5.3.2 Subpart B - Bleached Papergrade Kraft and Soda Subcategory

Commenters on the proposed rule indicated that EPA should retain the existing subcategorization scheme which was based on an evaluation of raw waste loads and flows. One

commenter further stated that if EPA insists on revising the subcategories, raw waste loads, product type, fiber furnish, and raw waste treatability must also be evaluated in addition to effluent loads.

In response, for the Bleached Papergrade Kraft and Soda Subcategory, EPA undertook an analysis of the relationship between conventional pollutant loading (BOD₅ and TSS) in raw wastewater and treated effluent. No soda mills were included in the analysis because none had more than 85 percent of their final production in the subcategory. (EPA selected a final production cut-off of 85 percent within a single subcategory for the wastewater from the mill to be considered representative of that subcategory's wastewater. This approach is described in the Technical Development Document for the proposed rule (2) and in "Selected Issues Concerning Development of Conventional Pollutant Control Options" (3).) Specific analyses performed are documented and described in "Analysis of the Relationship Between Conventional Pollutant Loadings in Raw Wastewater and in Treated Effluent at Papergrade Kraft Mills" (4). The findings of this analysis include:

- The distribution of final effluent and raw wastewater BOD₅ and TSS loads support EPA's consolidation of the four current papergrade kraft and soda subcategories into a single subcategory;
- Final effluent conventional pollutant loads are <u>not</u> dependent on raw wastewater conventional pollutant loads;
- Final effluent conventional pollutant loads <u>are</u> dependent on treatment system removal efficiencies; and
- The data support EPA's assumption and demonstrate that the long-term average BOD₅ and TSS performance levels are achievable, regardless of raw wastewater loads.

The purpose of industry subcategorization is to provide a mechanism for addressing variations among raw materials, processes, products, and other parameters that can result in distinct effluent characteristics. Regulation of a category by subcategory ensures that each subcategory has a uniform set of effluent limitations that take into account technical achievability and economic impacts unique to that subcategory. EPA considered the processes, raw materials, wastewater treatability, and other factors unique to bleached papergrade kraft and soda mills as the basis for combining bleached papergrade kraft and soda mills in a unique subcategory separate from other pulping processes (e.g., papergrade sulfite and dissolving kraft and sulfite processes).

EPA evaluated whether additional subcategory segmentation was appropriate for development of effluent limitations guidelines and standards for toxic and nonconventional pollutants based primarily on process changes (e.g., BAT and PSES). EPA considered further segmentation of the Bleached Papergrade Kraft and Soda Subcategory by product brightness

(high versus low) and fiber furnish (hardwood versus softwood) because these factors may influence the technical feasibility of bleaching process technologies. EPA decided not to further segment the Bleached Papergrade Kraft and Soda Subcategory by product brightness because available data do not demonstrate that variation in this parameter results in significant differences in effluent characteristics. Moreover, at some mills, final product characteristics vary sufficiently (on a day-to-day basis) to make permitting and compliance impracticable. EPA was also concerned that mills might strive for higher brightness than their product required in order to qualify for less stringent limits, with the unintended result of having mills use more rather than less bleaching chemicals and hence discharging more pollution than they otherwise would.

EPA also considered fiber furnish (hardwood versus softwood) as a basis for further segmenting the Bleached Papergrade Kraft and Soda Subcategory. For toxic and nonconventional pollutants with compliance points at the bleach plant, EPA found no difference in achievability of limitations due to fiber furnish. However, for the bulk parameter adsorbable organic halides (AOX) with compliance point at the end-of-pipe, EPA found higher effluent loadings for softwood mills than for hardwood mills. EPA set limitations for AOX based on data for softwood mills to ensure that the limitations would be achievable for all furnishes. Since many mills pulp both hardwood in variable combinations, or "swing" between hardwood and softwood, effluent limitations based on fiber furnish would be very difficult to administer. For this reason, EPA found it unnecessary and inappropriate to further segment the Bleached Papergrade Kraft and Soda Subcategory by fiber furnish.

5.3.3 Subpart E - Papergrade Sulfite Subcategory

Several comments were submitted concerning the feasibility of "totally chlorine-free" (TCF) technology-based limits for certain sulfite pulping processes and products. Specifically, comments indicated that TCF bleaching processes are not technically feasible for manufacture of ammonium-based papergrade sulfite pulp from softwood and for manufacture of specialty papergrade sulfite products such as pulps for photographic papers and plastic molding products.

After reviewing the comments, EPA concurs that additional segmentation of the Papergrade Sulfite Subcategory is necessary to better reflect product considerations, the variation of manufacturing processes, and the demonstration of pollution prevention process changes within the category for the purpose of establishing BAT, PSES, NSPS, and PSNS. See "Segmenting the Papergrade Sulfide Subcategory" (5) for additional information concerning EPA's rationale for segmenting the Papergrade Sulfite Subcategory. The segments for the Papergrade Sulfite Subcategory are:

(a) Production of pulp and paper at papergrade sulfite mills that use an acidic cooking liquor of calcium, magnesium, or sodium sulfite unless those mills are specialty-grade sulfite mills.

- (b) Production of pulp and paper at papergrade sulfite mills that use an acidic cooking liquor of ammonium sulfite, unless those mills are specialty-grade sulfite mills.
- (c) Production of pulp and paper at specialty-grade sulfite mills. Specialty-grade sulfite mills are those mills where (1) 25 percent or more of production is characterized by pulp with a high percentage of alpha cellulose and high brightness sufficient to produce end products such as plastic molding compounds, saturating and laminating products, and photographic papers; or (2) those mills where 50 percent or more of production is 91 ISO (International Organization for Standardization) units brightness and above.

EPA is not revising NSPS for conventional pollutants for the Papergrade Sulfite Subcategory. Because the NSPS for conventional pollutants for former Subparts J and U were the same, EPA has recodified these standards in a single table for Subpart E (without distinguishing between the former subparts in the form of segments).

5.4 <u>References</u>

- Comment Response Document, Volume I, "Selected Issues Concerning Subcategorization." U.S. Environmental Protection Agency, Washington DC, Record Section 30.11, DCN 14497, 1997.
- Development Document for Proposed Effluent Limitations Guidelines and Standards for the Pulp, Paper, and Paperboard Point Source Category. EPA-821-R-93-019, U.S. Environmental Protection Agency, Washington DC, October 1993.
- 3. <u>Comment Response Document</u>, Volume I, "Selected Issues Concerning Development of Conventional Pollutant Control Options." U.S. Environmental Protection Agency, Washington DC, Record Section 30.11, DCN 14497, 1997.
- 4. Radian Corporation. <u>Analysis of the Relationship Between Conventional Pollutant Loadings in Raw Wastewater and in Treated Effluent at Papergrade Kraft Mills</u>. Herndon, Virginia, Record Section 22.1, DCN 14039, November 16, 1995.
- 5. <u>Comment Response Document</u>, Volume I, "Segmenting the Papergrade Sulfite Subcategory." U.S. Environmental Protection Agency, Washington DC, Record Section 30.11, DCN 14497, 1997.

SECTION 6

WATER USE AND WASTEWATER CHARACTERISTICS

6.1 Introduction

Section 6.0 of the TDD describes water use and wastewater recycle practices, and the general characteristics of wastewater at mills that manufacture pulp, paper, and paperboard in the U.S. This information was gathered in EPA's 1990 National Census Questionnaire of the industry. All pulp and papermaking processes use water; in fact, the pulp and paper industry is the largest industrial process water user in the U.S. Except as noted below, EPA believes that the information presented in Section 6.0 of the TDD is still representative of the industry today. This section discusses specific topics related to water use.

Water use in the industry decreased approximately 30 percent between 1975 and 1990, reflecting significant effort by the industry to reduce consumption and increase wastewater reuse and recycle (1). EPA believes that this trend has continued because mill modernizations have occurred and continue to occur. These projects generally include the installation of equipment that uses water more efficiently. The total effluent flow from an integrated bleached kraft mill is normally between about 50 to 150 m³/kkg of pulp produced, although a few mills discharge significantly lower or higher flows (2). In 1995, the average U.S. bleached kraft and soda mill discharged approximately 95 m³/kkg of pulp (3).

6.2 Mill Water Use - Bleach Plant Effluent Portion of Final Effluent

The final rule preamble and Section 8.2.3 of this document set forth EPA's reasons for regulating some pollutants at the bleach plant effluent rather than at the final effluent discharge to receiving waters. One reason is that most of the regulated chlorinated compounds are not present at detectable concentrations in the final effluent, and may or may not be present at detectable concentrations in the bleach plant effluent. Because the bleach plant effluent flow rate is a fraction of the influent to treatment flow rate (which is assumed to be the same as the final effluent flow rate for this analysis), EPA is concerned that the dilution of the bleach plant effluent in the final effluent will make it more difficult to detect the regulated chlorinated compounds in the final effluent. This section describes the fraction of the final effluent that is composed of bleach plant effluent.

The fraction of the final effluent that is composed of bleach plant effluent is described in various references as shown below. Although the figures listed in each reference differ, they agree that the final effluent is composed of a significant fraction of bleach plant effluent as well as other wastewaters from other areas of the mill. The data are believed to be similar for bleached papergrade kraft mills and for papergrade sulfite mills.

Source	Bleach Plant Effluent Flow Percentage of Final Effluent Flow
EPA Sampling Database (derived from bleached papergrade kraft mills) (4)	7% to 43%
Technical Development Document, (1990 Industry Census Questionnaire) (5)	30 to 50%
Average of Bleached Papergrade Kraft Mills	30%
Average of Papergrade Sulfite Mills	35%
Water Use Reduction in the Pulp and Paper Industry (6)	50%
Pulp Bleaching - Principles and Practice (7)	50 to 70%

The figures derived from the EPA sampling database are discussed in more detail below but the other references provide little more information than is listed in the table. The EPA sampling database contains information from mills sampled by EPA, and information supplied by NCASI and individual mills.

The mills in the EPA sampling database were divided into two groups: mills that make market pulp only, and mills that make pulp and paper. The amount of bleach plant effluent in the final effluent for market pulp mills ranged from 21 to 43 percent (among nine mills). For the pulp and paper mills the range was 7 to 38 percent (among nine mills). An integrated mill has more wastewater sources, mainly from the paper making operations, so the bleach plant effluent proportion is smaller. The lowest values in each group (7 and 21 percent) were reported by mills that make unbleached pulp in addition to bleached pulp. The mills included in this analysis used a variety of bleaching sequences. The values for the nine mills using elemental chlorine-free bleaching sequences to make only bleached pulp were 30 to 43 percent.

6.3 Mill Water Use For Option A and Option B Mills

Of the mills included in the EPA sampling database, mills using extended cooking and/or oxygen delignification (Option B technologies) generally discharged less wastewater than mills using conventional cooking (Option A technology). In addition, those mills using totally chlorine-free bleaching discharged less wastewater than the mills using elemental chlorine-free bleaching sequences, because in chlorine-free bleaching processes, the bleach plant filtrates are returned to the recovery system. Several reasons exist for these differences. The following table summarizes the average production-normalized bleach plant flow rates that EPA calculated using its sampling database. The following production-normalized bleach plant flow rates were used to calculate some of the pollutant loadings and reductions described in Section 9.0.

Production-Normalized Kraft Bleach Plant Flow Rates^a

	Hardwo	od Lines	Softwoo	d Lines
Type of Mill ^b	Average (m³/kkg)	No. Of Lines	Average (m³/kkg)	No. Of Lines
Mills Without EC or OD	24.7	12	37.1	13
Mills With EC and/or OD	19.7	4	24.7	12
TCF Mills	11.6	1	18.3	2

^aThe average flow rates presented in this table were derived from bleached papergrade kraft mills.

Although retrofitting an oxygen delignification system (which would be a practical necessity for compliance with Option B) has no direct effect on effluent flows by itself, the data presented above indicate that mills with extended cooking and/or oxygen delignification have lower bleach plant flows than mills with conventional pulping. Several possible reasons exist for the lower flow. Some mills have reported reductions in effluent flow due to oxygen delignification projects because it is normal practice to close the screen room process and return these filtrates to the recovery cycle when oxygen delignification is installed. In some cases, when unbleached pulp kappa number-into-bleaching is reduced, it is possible to retire one or two complete bleaching stages (e.g., convert a C/DEoDED bleach plant to OD-DEopD). Such action could reduce effluent flows by about 15 m³/kkg pulp. In rare cases, oxygen delignification will result in some water conservation if lower unbleached pulp kappa number-into-bleaching allows the use of reduced wash water flow in the first bleaching stage.

The following discussion explains several reasons why EPA expects mills to continue to reduce effluent flow rates. Other changes in effluent flow rates as a result of the promulgated regulations are discussed in Section 11.3.

Water use in the industry decreased approximately 30 percent between 1975 and 1990 (1), reflecting significant effort by the industry to reduce consumption and increase wastewater reuse and recycle. These reductions may have resulted from specifically planned water conservation projects or they may have been secondary benefits of other mill modernization projects. During mill renovation, new equipment is not installed in isolation. Instead, it is common practice to modernize the entire mill area involved with the new equipment, at least to some extent. Modern equipment is generally designed to conserve water more effectively than older designs. Many details can be involved, such as the replacement of packing on shafts with modern mechanical seals that use little or no water, or reduction in cooling water requirements by more efficient design and increased use of cooling towers with subsequent recycle. These modifications will generally reduce effluent discharges, but it is difficult to provide realistic numeric estimates.

^bEC = extended cooking, OD = oxygen delignification, TCF = totally chlorine-free bleaching

Two elements of the two BAT options that will reduce effluent flows directly are closing screen rooms and implementing BMPs. The application of current engineering practices to the design of new systems and equipment will result in conservation of water. The greatest improvements are likely to be seen in mills currently using relatively high quantities of water.

The kappa number of unbleached pulp entering the bleach plant is reduced by employing two types of extended delignification, extended cooking (EC) and oxygen delignification (OD). Mills that have recently installed EC and/or OD have also made related improvements. For example, new or upgraded washers use water more efficiently and may therefore generate less wastewater.

When upgrading the first chlorine/chlorine dioxide stage to high or 100 percent chlorine dioxide substitution for chlorine, it is common to convert from low consistency operation to medium consistency, or increase the use of recycled bleach filtrates for pulp dilution to raise the temperature without incurring the cost of direct steam heating. These changes can lead to an effluent reduction of about 12 m³/kkg pulp in softwood mills and 5 m³/kkg in hardwood mills. Such improvements are most likely to be made in mills which have high effluent flows.

6.4 Definition of Process Wastewater

The effluent limitations guidelines and standards for the pulp and paper industry are applicable to discharges of process wastewaters directly associated with the manufacturing of pulp and paper. In 1993, EPA proposed a definition of process wastewater as any water which during manufacturing or processing comes into direct contact with or results from the production or use of any raw material, intermediate product, finished product, byproduct, or waste product. The proposed definition also specifically included boiler blowdown, wastewaters from water treatment and other utility operations, blowdown from high rate (e.g., greater than 98 percent) recycled non-contact cooling water systems to the extent they are mixed and co-treated with other process wastewaters, and stormwaters from the immediate process areas to the extent they are mixed and co-treated with other process wastewaters. The proposed definition specifically stated that contaminated groundwaters from on-site or off-site groundwater remediation projects are not considered process wastewaters. Separate permitting was proposed to be required for the discharge of such groundwaters.

The proposed definition also specifically excluded certain process materials from the definition of process wastewater. These process materials included: green liquor at any liquor solids level, white liquor at any liquor solids level, black liquor at any liquor solids level resulting from processing knots and screen rejects, black liquor after any degree of concentration in the kraft or soda chemical recovery process, reconstituted sulfite and semi-chemical pulping liquors prior to use, any pulping liquor at any liquor solids level resulting from spills or intentional diversions from the process, lime mud and magnesium oxide, pulp stock, bleach chemical solutions prior to use, and paper making additives prior to use (e.g., alum, starch and size, clays and coatings). Because these materials were excluded from the proposed definition of

process wastewater, they would have been prohibited from discharge into POTWs or waters of the United States without a National Pollutant Discharge Elimination System (NPDES) permit and effluent limitation or other authorization.

In response to the comments opposing the exclusion of these process materials (8), EPA revised the proposed definition of process wastewaters to eliminate the exclusion of the named process materials (40 CFR Part 430.01(m)). As the commenters contended, the proposed language would have effectively required "closed-cycle" mills, which was not EPA's intent. The proposed language was intended to prevent discharge of process materials during clean up in preparation for permanent mill closure. EPA's definition continues to specify that process wastewater is generated "during manufacturing or processing." Thus, the definition of process wastewater as promulgated today does not allow for discharges from a mill that is not engaged in manufacturing. Any mill wishing authorization to discharge in this manner must obtain authorization in an NPDES permit or individual control mechanism administered by a POTW.

The distinction that process wastewater is generated "during manufacturing or processing" should not be taken to exclude wastewaters generated during routine maintenance, including maintenance during a scheduled temporary mill shut-down. Maintenance wastewaters were not explicitly excluded from the definition of process wastewater at proposal, nor are they excluded from the definition finally promulgated. Wastewaters generated during routine maintenance are a result of pulp manufacturing processes and as such are included in the definition of process wastewater. Many mills commingle leachates from landfills receiving wastes associated with the processing or manufacturing operations. Therefore, EPA also has included these leachate wastewaters in the definition of process wastewaters.

6.5 <u>Use of Biocides</u>

The existing BAT regulations for Subparts G, H, I, J, P, and U (now the Bleached Papergrade Kraft and Soda and Papergrade Sulfite subcategories) establish effluent limitations guidelines and standards for pentachlorophenol and trichlorophenol when used as biocides. One way for dischargers to comply with these limitations is to certify that they do not use these compounds as biocides. Using the data collected in the 1990 National Census Questionnaire, EPA compared the names of biocide products reported as used by pulp mills in the Bleached Papergrade Kraft and Soda and Papergrade Sulfite subcategories with readily available information from the Office of Pesticide Programs to determine if these products contain pentachlorophenol or trichlorophenol. EPA was unable to identify any biocide products used by those pulp mills that contain these chemicals. Therefore, EPA expects that mills in these subcategories will be able to comply with these limitations by certifying that they do not use these compounds as biocides.

6.6 <u>References</u>

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SECTION 7

POLLUTION PREVENTION AND WASTEWATER TREATMENT TECHNOLOGIES

7.1 Introduction

This section describes technologies that are in use at pulp, paper, and paperboard mills to prevent the formation of wastewater pollutants or reduce the discharge of wastewater pollutants. Various combinations of these technologies were considered as the basis for the effluent limitations guidelines and standards for the industry.

Two major approaches may be used to improve effluent quality at pulp, paper, and paperboard mills: (a) in-process technology changes and controls to prevent or reduce the formation of wastewater pollutants of concern, and (b) end-of-pipe wastewater treatment technologies to remove pollutants from process wastewaters prior to discharge.

The Agency has defined pollution prevention as source reduction and other practices that reduce or eliminate the formation of pollutants. Source reduction includes any practice that reduces the amount of any hazardous substance or pollutant entering any waste stream or otherwise released into the environment, or any practice that reduces the hazards to public health and the environment associated with the release of such pollutants. Such practices may include equipment or technology modifications; process or procedure modifications; reformulation or redesign of products; substitution of raw materials; and improvements in housekeeping, maintenance, training, and inventory control. Other pollution prevention practices include increased efficiency in the use of raw materials, energy, water, and other resources.

The Agency has developed a model pollution prevention plan for the pulp and paper industry as part of the Agency's effort to encourage pollution prevention programs in U.S. industries. The model plan is discussed in a series of reports:

Pollution Prevention Opportunity Assessment and Implementation Plan for Simpson Tacoma Kraft Company, Tacoma, Washington (1);

Model Pollution Prevention Plan for the Kraft Segment of the Pulp and Paper Industry (2); and

Pollution Prevention for the Kraft Pulp and Paper Industry, Bibliography (3).

Pollution-preventing process changes may be implemented in the pulping, bleaching, chemical recovery, and papermaking areas of a mill. Many of the in-process controls that prevent or reduce wastewater pollution also result in improved product quality and/or fiber yield, as well as reduced operating costs through more efficient use of process materials and prevention and control of leaks and spills of spent pulping liquor, soap, and turpentine. Sections

7.2 and 7.3 describe applicable pollution prevention controls and technologies for the industry. These sections also provide information on the performance of each technology and the number of mills using each technology.

Additional information on pollution prevention technologies for the pulp and paper industry is available in these EPA documents:

Summary of Technologies for the Control and Reduction of Chlorinated Organics from the Bleached Chemical Pulping Subcategories of the Pulp and Paper Industry (4);

Pollution Prevention Technologies for the Bleached Kraft Segment of the U.S. Pulp and Paper Industry (5); and

Technical Development Document for the Pulp, Paper, and Paperboard Category Effluent Limitations Guidelines, Pretreatment Standards, and New Source Performance Standards (6).

End-of-pipe wastewater treatment includes physical, chemical, and biological processes that remove pollutants from mill effluent prior to discharge to a receiving stream or POTW. Section 7.4 describes end-of-pipe wastewater treatment technologies applicable to the industry.

7.2 <u>Pollution Prevention Controls Used in Pulping and Delignification Processes</u>

This section describes applicable technologies for reducing and preventing pollutant discharges from the pulping area of a chemical pulp mill. Pulping area processes include chipping, cooking, pulp washing, and screening. Pollution prevention technologies applicable to pulping area processes include chip quality control, use of dioxin precursor-free defoamers and pitch dispersants, extended cooking, effective brown stock washing, closing the screen room, oxygen delignification, steam stripping of condensates, and spent pulping liquor spill prevention and control.

7.2.1 Chip Quality Control

Chip thickness control is an important component of improving yield, reducing bleaching chemical requirements, and optimizing pulp quality. Chip thickness can be controlled by close control of chipping equipment tolerances or the use of chip thickness screens.

In preparation for chemical pulping, wood is reduced to chips approximately 2 to 5 millimeters thick and 10 to 30 millimeters long. Some mills use chips obtained from an off-site source such as a sawmill, although most mills perform at least some chipping on site. Several chipper designs are in use today, but the most common is the flywheel-type disc chipper, in which

logs are fed to one side of the disc at a pre-determined angle through a vertical directing chute.

After chipping, the chips pass a set of vibratory screens to separate chips of acceptable length and width from fines and oversized pieces. Oversized chips are rechipped, and fines are usually burned in an on-site hog fuel boiler.

Good quality chipping and screening equipment provides a uniform supply of chips to the digester, leading to more uniform cooking and reduced digester chemical consumption. The uniform pulp produced results in less variation in bleach plant feed and better control of the bleaching process, which reduces overbleaching of the pulp to remove shives and colored fiber. The effluent quality from the bleach plant is improved because when overbleaching is avoided, lower levels of chlorinated organics are formed. A more uniform pulp also reduces the amount of rejects from screening following brown stock washing.

Mills can improve the quality of chips going to the digester in several ways. Mills that receive chips from an off-site source can develop a chipping quality control program for suppliers to ensure that uniform, high-quality chips are received. Mills that chip on site can closely monitor the operation of the chipper to maintain optimum settings (e.g., consistent and effective blade settings) in order to produce chips of consistent size. This approach minimizes the quantity of off-specification chips produced, and eliminates the need for chip thickness screens (7).

Mills can also provide uniform chip dimensions with chip thickness screens. Chip thickness screens are rotating disc screens that separate overly thick chips, which are then sliced or crushed to the desired thickness for pulping. Chip thickness screening also removes knots and compression wood, in which dioxin precursors are reported to be concentrated (8). Providing chips of uniform thickness, free of knots and compression wood, results in improved pulping, reduced screen rejects, and improved bleaching, and may also reduce the load on the mill's wastewater treatment system. When knots and compression wood are removed prior to cooking, they are typically burned in the mill's power boiler. If these components are instead removed from the pulp by screening after cooking, they may be sent to the wastewater treatment system. New mills in the U.S. typically use chip thickness screening and many existing mills have installed chip thickness screens, usually as part of an overall woodyard or pulp mill upgrade. Therefore, EPA considers chip quality control to be a part of the baseline technology used today at bleached papergrade kraft mills and additional cost for this technology has not been included in the BAT/PSES options.

7.2.2 Defoamers and Pitch Dispersants

Defoamers are used to break and inhibit the formation of black liquor surface foam formed when air is entrained in the pulp during brown stock washing. Pitch dispersants are added to pulp to prevent wood resins and fatty acids from depositing on the paper at the paper machine. Both of these chemical additives are introduced into the pulp flow prior to brown stock washing and are carried with the pulp into the bleach plant. Defoamers and pitch dispersants have been

shown to contain the chlorinated dibenzo-p-dioxin (CDD) and chlorinated dibenzofuran (CDF) precursors dibenzo-p-dioxin (DBD) and dibenzofuran (DBF) (5,10). In the first (chlorine or chlorine dioxide) stage of bleaching, the DBD and DBF are chlorinated to form 2,3,7,8-TCDD and 2,3,7,8-TCDF.

Defoamers can be mineral oil based or water based. Mineral oil-based defoamers are a blend of 90 percent oil and 10 percent additives. Defoamers made from re-refined oil are particularly high in DBF concentration (11). DBD and DBF can be essentially eliminated from defoamer oils (i.e., to a level of less than 1 ppb of both) by using two-stage severe hydrotreating technology (11). Alternatively, completely oil-free defoamers that do not contain CDD and CDF precursors may be used (12). Switching to non-contaminated defoamers can contribute to reducing the content of 2,3,7,8-TCDF in bleached pulp and in mill effluent by at least 90 percent (13). The Agency believes that the U.S. pulp industry has generally converted to the use of precursor-free additives.

As evidenced by the drop in measured TCDD and TCDF discharges from bleaching pulp mills, use of either water-based defoamers or defoamers made with precursor-free mineral oils has been common industry practice since the early 1990s. At that time, it became widely known in the industry that use of precursor-free defoamers in the brown stock or bleach plant areas substantially reduces the dioxin formed in bleaching. Consequently, EPA assumes use of precursor-free defoamers to be part of the baseline technology used today at bleached papergrade kraft mills and costs have not been included in the BAT/PSES options.

7.2.3 Extended Cooking

At chemical pulping mills, wood chips or a non-wood fiber furnish are cooked in a chemical solution in a digester at elevated temperature and pressure to dissolve the lignin that holds the cellulose fibers together. Chemical pulping occurs in either a batch or continuous digester system.

The most common continuous digester is the vertical downflow type. The wood chips are preheated in a steaming vessel to remove air and some of the volatile wood constituents before the chips enter the digester. The chips are mixed with the cooking liquor and are fed into the top of the digester so that they move downward by gravity through the tower. The hydraulic pressure in the tower is kept at approximately 1,140 kPa (165 psi). After the chips have been impregnated with liquor, the temperature is raised to approximately 105 to 130 time of one to one and a half hours, until the pulping reaction is complete. The reaction is stopped in the lower region of the tower, where diffusion washing of the pulp is carried out, normally using a countercurrent flow of the filtrate from the first brown stock washer. The pulp is blown from the bottom of the digester at about 1,380 kPa (200 psi) to a tank at atmospheric pressure.

For batch cooking, a mill normally uses several vessels. Mills in the U.S. with batch digesters have reported using anywhere from 3 to 24 vessels. Wood chips and cooking

liquor are added simultaneously to the top of the digester, after which the digester is sealed and raised to a target operating pressure of approximately 700 to 900 kPa (102 to 131 psi) and temperature of approximately 170

cooking for one to two hours, the pulp is blown into an atmospheric tank, from which it is pumped to the brown stock washing system. Usually a mill staggers the digester cycles to maintain a continuous flow of pulp through its washing and pulping sections.

The continuous process produces pulp at a consistent rate and with lower energy requirements; however, a batch pulping system enables a mill to pulp several different grades at once by using different digesters for different pulping conditions or fiber furnishes. Since the continuous process was commercialized in the 1950s, the amount of chemical pulp produced by continuous digesters has increased. Most new installations are now continuous systems.

Chemical pulp mills that bleach must remove enough residual lignin from the pulp prior to bleaching to achieve their required final pulp brightness. The kappa number (a measure of a pulp's lignin content) of the pulp entering the bleach plant dictates the amount of bleaching chemicals needed. Since decreasing bleaching chemical use lowers both the cost for bleaching chemicals and the environmental impact of the effluent from the bleach plant, it is generally desirable for mills that bleach to lower the prebleaching kappa number as much as possible, without seriously affecting pulp yield and strength.

Through work done by the Swedish Forest Products Research Institute (STFI) in the late 1970s (14), the concept of "extended cooking" for papergrade kraft pulps was developed and commercialized in the late 1980s. Extended cooking enables a mill to lower the kappa number of the pulp entering the bleach plant further than is possible with a traditional kraft pulping digester, while increasing pulp strength and maintaining or increasing pulp yield. During extended cooking, the pulp is mixed with the cooking liquor for a longer time than in traditional cooking, under modified temperature and alkalinity conditions. The process can be performed using either a batch or continuous pulping system. Thirteen of the 86 mills in the Bleached Papergrade Kraft and Soda Subcategory used extended cooking as of mid-1995. Extended cooking is not typically used for papergrade kraft pulps that will not be bleached, because achieving a low kappa number out of the digester is not as important as it is for pulps that will be bleached.

In 1992, approximately 11 million kkg/year of kraft pulp was produced worldwide using extended cooking (15). This figure represents about 20 percent of world bleached kraft capacity. Figure 7-1 shows the increase in the amount of kraft pulp produced by extended cooking from 1983 through 1992. Capacities shown are as reported by mills and vendors, and have been normalized to air dry kkg/day. Extended cooking for dissolving kraft and sulfite pulps has not been demonstrated on an industrial scale.

The types of continuous extended cooking processes most commonly used in the U.S. are the Modified Continuous Cooking (MCC®) developed by Kamyr Inc. and Kamyr AB and Iso Thermal Cooking (ITC®) process developed by Kvaerner, and Extended Modified

Continuous Cooking (EMCC®) processes developed by Kamyr Inc. Figure 7-2 shows a typical EMCC® installation. These processes are similar, in that fresh cooking liquor, comprised of sodium hydroxide and sodium sulfide, is added at several points in the digester, instead of at just one point as with traditional continuous cooking. More lignin is dissolved with these processes than is dissolved in the traditional digester, because the active chemical concentration is kept more uniform throughout the cooking process. At the same time, less damage is done to the wood fiber cellulose, because a high initial cooking liquor concentration is avoided. The resulting pulp is stronger and has a lower kappa number than traditional pulps, while the pulp yield is maintained.

Extended cooking in batch digesters yields similar results. Two systems are available commercially: the Rapid Displacement Heating (RDH®) System, sold by Beloit Inc., the Super Batch® System, sold by Sunds Defibrator, Inc., and VISBATCH® and ENERBATCH®, sold by Voest-Alpine. These processes maintain a more uniform cooking liquor concentration throughout the cook than traditional batch cooking. The wood chips are initially impregnated with warm black liquor under pressure to remove air in the chips. The warm black liquor is then displaced with hot black liquor and white liquor to begin the cook. After cooking, the spent cooking liquor is displaced with wash liquor from the first brown stock washer. The spent cooking liquor becomes the warm black liquor used for impregnation during another cook. The batch extended cooking process requires several large holding tanks to store liquor between the various stages of the cooking process, and many older mills do not have the space to install a batch extended cooking system. Most of the extended cooking installations in the world are continuous rather than batch, although several batch systems have recently been installed.

The unbleached kappa number of softwood kraft pulps typically ranges from 30 to 32 for traditional cooking. Extended cooking by either the continuous or batch processes can achieve softwood pulp unbleached kappa numbers ranging from 12 to 18. For hardwood kraft pulps, the unbleached kappa number of approximately 20 for traditional cooking can be reduced to 8 to 10 using extended cooking (5). As explained in Section 8, EPA has used higher kappa number targets for the development of the regulatory options.

7.2.4 Effective Brown Stock Washing

In a chemical pulping mill, after the pulp leaves the digester it is cleaned through a series of knotters, screens, and countercurrent washers to remove impurities and uncooked fiber and to recover as much spent cooking liquor as possible. In brown stock washing, spent pulping chemicals, along with any dissolved wood components, are separated from the pulp and sent to the recovery boiler for recovery of chemicals and energy (steam generation). Effective brown stock washing minimizes the amount of pulping liquor carried over to the bleach plant with the pulp. The mill's effluent quality is also improved because residual black liquor that is carried over to the bleach plant includes unchlorinated toxic substances, some of which appear to resist degradation in biological treatment plants (16). If chlorine-based bleaching chemicals are used,

the organic compounds that are carried over with the pulp to the bleach plant also react with the bleaching chemicals and, therefore, increase the mill's effluent load of chlorinated organics.

Effective brown stock washing also reduces the amount of bleaching chemicals required to bleach the pulp to a given brightness, because well-washed pulp carries less organic material, which competes with the pulp fiber for reaction with the bleaching chemicals. Finally, effective brown stock washing is essential for satisfactory operation of an oxygen delignification system.

Mills try to minimize the amount of water used for brown stock washing, because all water added at this stage is typically evaporated in the black liquor recovery cycle. Although using more water increases the removal of pulping liquor and dissolved organic material from the pulp, the maximum amount of water that can be used depends on the capacity of the black liquor evaporators and the additional energy requirements necessary to evaporate more black liquor.

Brown stock washing effectiveness at kraft mills is conventionally expressed as saltcake (Na₂SO₄) loss per mass of pulp, and is considered to be effective if the washing loss is less than 10 kg Na₂SO₄/kkg of pulp (17,18,19). A loss of less than 10 kg Na₂SO₄/kkg is approximately equivalent to 99 percent recovery of spent pulping chemicals. The average washing loss for the Bleached Papergrade Kraft and Soda Subcategory was 13.5 kg Na₂SO₄/kkg in 1989, as reported in the 1990 census questionnaire. This washing loss is much lower than losses were ten years ago.

The traditional method of pulp washing using a rotary vacuum drum washer has been supplemented or replaced in many mills with other, high-efficiency washers, including pressure diffusion washers, belt washers, and presses of various types. All are capable of providing well-washed pulp.

Pressure diffusion washers are enclosed and operate at elevated pressure and temperature, resulting in good washing efficiency. The pulp enters a pressure diffusion washer at the top and moves downward as a fiber mat between the stationary central body of the washer and the moving perforated cylindrical screen surrounding it. The wash water flows from the center of the washer through the pulp mat and outer screen, and is extracted continuously from the system. The pulp continues through the vessel and is removed at the bottom. Pressure diffusion washers require relatively less floor space than other types of washers and are therefore often selected for upgrading a mill's washing system where little space is available.

In a belt washer, the pulp flows onto an endless moving horizontal filter cloth and is drawn off at the opposite end. Wash water is applied to the top of the pulp mat and is drawn through the pulp by vacuum boxes located beneath the cloth. Each wash water addition point is considered to be one "stage" of washing, and the wash water moves countercurrently from the final stage through to the first stage on the belt. A belt washer can provide up to seven stages of washing. The system can be enclosed to minimize air emissions. Belt washers are not currently

used to incrementally increase brown stock washing capacity, but are efficient systems for replacing an entire washing line.

A wash press consists of a cylindrical washer and a press roll. Pulp that is washed in a wash press leaves the system at a higher consistency than with other washing systems. The geometric configuration of the cylindrical washer causes the pulp to be dewatered during washing, because the pulp is forced into a smaller space and ultimately passes through a nip between the washing cylinder and the press roll. Instead of leaving the washer at the usual consistency of between 10 and 15 percent solids, the pulp mat leaves at a consistency of between 30 and 40 percent. This type of washer is beneficial when high consistency is required downstream of the brown stock washing area.

7.2.5 Closed Screen Room Operation

After brown stock washing, pulp is usually screened to remove oversized particles. The pulp is first diluted with fresh water, screened using gravity or pressure screens, and then thickened in a decker to an appropriate consistency for the next process operation. In an open screen room, the filtrate from the decker goes to the sewer. This sewered stream carries residual organics and cooking liquor solids from the pulping operation. Closing the screen room eliminates the overflow of decker filtrate to the sewer. This operation optimizes the water balance around the washing and screening operations, because all of the decker filtrate is reused as dilution water for the screening operation, or as brown stock wash water. Residual organics and cooking liquor are thus returned to the chemical recovery cycle. Implementing closed screening effectively allows the decker to be used as an extra stage of brown stock washing.

The closed screen room concept has been discussed in literature for many years. The use of closed screening lowers the overall waste load to the mill wastewater treatment system, including the chemical oxygen demand (COD) load. Closed screening is standard equipment for mills using oxygen delignification because it is an integral part of the brown stock area in which an appropriate flow balance must be maintained for the efficient operation of oxygen delignification. The use of closed screening is becoming the common industry practice. Based on information collected by EPA in mid-1995, 44 of 86 bleached papergrade kraft mills in the United States used closed screen rooms.

The ability to operate the screen room as a closed process depends on a systematic optimization of the pulping, washing, screening, and liquor recovery cycles, and the type of washing and screening equipment available. Effective brown stock washing should be used to minimize the amount of cooking liquor solids carried to the screening operation. In addition, many mills are replacing gravity flow screens with pressure screens to prevent air entrainment and resultant foaming problems (20).

7.2.6 Oxygen Delignification

Oxygen delignification uses oxygen gas to remove lignin from pulp after brown stock washing and prior to bleaching. Using oxygen delignification between the kraft or sulfite pulping processes and the bleach plant results in lower bleaching chemical demands than a traditional bleaching sequence, because the unbleached kappa number drops by approximately 50 percent and the subsequent bleaching chemical requirements also drop in a relative manner (5). In addition, bleaching to a particular brightness can often be accomplished using fewer bleaching stages than a traditional bleach line if oxygen delignification is used prior to bleaching. Decreased bleaching chemical use reduces pollutant levels in the mill's bleach plant effluent. Although the operation of an oxygen delignification system in itself does not decrease the effluent flow from the bleach plant, it can lessen water use if older, less efficient bleaching towers are bypassed and if filtrates are sent to recovery boilers.

Over one-half of the world's bleached kraft production is subject to oxygen delignification. This number includes 100 percent of mills in Sweden and Japan, all but one mill in Finland, and essentially all new mills built worldwide in the last 10 years. As of mid-1995, 22 mills in the Bleached Papergrade Kraft and Soda Subcategory reported using oxygen delignification. The amount of bleached papergrade kraft pulp produced by these mills using oxygen delignification represented approximately 30 percent of the total U.S. production. One mill in the Papergrade Sulfite Subcategory reported using oxygen delignification. Figure 7-3 illustrates the rate of increase in the use of oxygen delignification systems in the U.S. and worldwide. Oxygen delignification has been adopted much more extensively in foreign mills than in U.S. mills, while U.S. mills have adopted extended cooking more rapidly than foreign mills.

Figures 7-4 and 7-5 show medium- and high-consistency oxygen delignification systems, respectively, both of which are in use today. In both cases, oxygen delignification must start with well-washed pulp, and magnesium salt (MgSO₄) must be added to protect the cellulose fibers from degradation. After oxygen delignification, the pulp must be washed well to remove organic material so that the subsequent bleaching stages can operate effectively.

High-consistency oxygen delignification is accomplished at a consistency of approximately 25 to 30 percent, which is attained using a press prior to the oxygen delignification tower. The pulp is then fed to a pressurized reactor into which oxygen and sodium hydroxide (or oxidized white liquor) are added. The pulp is fluffed using baffles inside the tower to achieve a more consistent reaction, and gaseous reaction products are purged from the vessel to avoid a fire hazard. Pulp degradation has been a problem with high-consistency systems, even though magnesium salt is added for pulp stabilization.

Medium-consistency oxygen delignification takes place at a consistency of between 10 and 20 percent, which is attained using a brown stock decker. The decker averts the need for the more expensive press that is required for a high-consistency oxygen delignification system.

Prior to entering the reaction tower, the pulp is mixed with oxygen and sodium hydroxide (or oxidized white liquor). Since fewer gaseous compounds are formed, the risk of fire is eliminated with the medium-consistency system. The medium-consistency system has less potential for pulp degradation than in a high-consistency system, but slightly less delignification occurs than with a high-consistency reaction due to a lower reaction rate.

The filtrate from the post-oxygen delignification washers is sent to the recovery boiler, marginally increasing the load on the boiler, but concurrently increasing the amount of recovered chemicals and energy (21). Recycling the filtrate from the oxygen delignification washers, rather than sending it to wastewater treatment, reduces the bleach plant effluent flow, load of BOD₅ by 30 to 50 percent, COD by 40 percent, color by approximately 60 percent, and chlorinated organics by approximately 35 to 50 percent (5,8). Currently, all kraft and sodium-based sulfite mills with oxygen delignification recycle the associated filtrate.

7.2.7 Steam Stripping

Wastewater streams in the pulping and chemical recovery areas of a chemical pulp mill contain organic and sulfur compounds that may be emitted to the air or conveyed to the wastewater treatment system. Condensate streams from evaporators, digester blow tanks, and turpentine recovery systems at kraft mills contain the highest loadings of these compounds, with evaporator condensate representing the major volume of pulping area condensate flow. Steam strippers are used to control air emissions of organic and sulfur compounds from pulping area condensate streams, and at the same time reduce the organic load of the stripped wastewater on the wastewater treatment system.

Steam stripping is a fractional distillation process that involves the direct contact of steam with wastewater. Figure 7-6 presents a schematic of a continuous steam stripper system. Wastewater is pumped into the top of the stripping column, and steam is injected near the bottom of the column. The column is typically equipped with perforated trays or packing to increase contact between the vapor and the liquid. Heat from the steam vaporizes the volatile compounds in the wastewater, which are carried out the top of the column with the steam. This overhead vapor stream is typically incinerated on site with attendant energy recovery (steam generation) (22). In the future, the overhead vapor stream may be concentrated or rectified to produce a methanol-rich stream that can be used to replace other fuels burned on site. Wastewater leaving the steam stripper passes through a heat exchanger to preheat the unstripped wastewater entering the steam stripper. The stripped wastewater is then discharged to the wastewater treatment system or reused in the mill for fresh hot water applications. The removal efficiency of volatile compounds is determined by the steam-to-feed ratio in the column. The steam stripper may be a stand-alone piece of equipment, or, at some mills, it may be integrated into the evaporator set.

A properly designed steam stripper can reduce the BOD₅ load to a mill's wastewater treatment system by removing organic compounds, primarily methanol, from the pulping area condensate streams. Mills that currently use steam stripping to reduce the load of organic constituents discharged to wastewater treatment report using steam-to-feed ratios ranging

from 145 to 215 kg/m³. A steam-to-feed ratio of 180 kg/m³ achieves approximately 90 percent removal of methanol. Total reduced sulfur (TRS) compounds can be removed at lower steam rates. Steam stripping is not part of the BAT/PSES model technology, but is part of MACT. Therefore, costs for steam stripping were incorporated in the basis for the MACT I standards rather than the BAT/PSES options. See the preamble at Section VI.A.

7.2.8 Spent Pulping Liquor Management, Spill Prevention, and Control

Mills that perform chemical or semi-chemical pulping of wood or other fibers generate spent pulping liquors that are generally either recovered in a chemical recovery system or treated in a wastewater treatment system. These mills may lose pulping liquor through spills, equipment leaks, and intentional diversions from the pulping and chemical recovery areas of the mill. Spills and intentional diversions of pulping liquor are a principal cause of upsets in biological wastewater treatment systems, the type of treatment system used at most chemical and semi-chemical pulp mills. Spent pulping liquor losses also increase the need for pulping liquor make-up chemicals, decrease energy generated from pulping liquor solids combustion, and increase hazardous air pollutant emissions.

Unintentional pulping liquor losses at pulp mills are most commonly caused by process upsets, equipment breakdowns, and tank overfillings. Maintenance and construction in a mill's pulping and chemical recovery areas may cause intentional diversions of pulping liquor to the wastewater treatment system. Spent pulping liquor may also be lost during normal mill operations, such as planned shutdowns and start-ups and pulp grade changes.

In addition to the potential harm to biological wastewater treatment systems and possible increased releases of toxic and hazardous substances associated with spills and other releases of spent pulping liquor, the discharge of substantial quantities of soap and turpentine has been shown to be extremely harmful to biological wastewater treatment systems and has resulted in violations of NPDES permit levels. The provision of secondary containment for turpentine storage tanks and other curbing, along with diversion and containment measures in soap and turpentine handling areas, constitute another element of a management program aimed at protecting wastewater treatment effectiveness and protecting the receiving waters.

Management programs, combined with engineered controls and monitoring systems, can prevent or control spent pulping liquor losses. These efforts should be both proactive to prevent pulping liquor losses and reactive to control spills after they have occurred.

Practices to prevent or control spent pulping liquor losses at chemical pulp mills include the following:

Management of process operations to minimize variability.

Preventative maintenance programs for equipment in spent pulping liquor service.

Automated spill detection, such as conductivity sensors in sewers in the pulping and chemical recovery areas.

Frequent operator surveillance of pulping and chemical recovery areas to quickly detect and repair leaks.

Secondary containment or annual integrity tests and high-level alarms on pulping liquor bulk storage tanks.

Secondary containment for turpentine storage tanks and other collection, containment, and control measures for soap and turpentine areas.

Spill collection systems for the pulping and chemical recovery areas with sufficient capacity to store collected spills and planned liquor diversions. The collected liquor may then be recovered in the chemical recovery system or slowly released to the wastewater treatment system at a rate that does not adversely impact the wastewater treatment system.

Mills with effective pulping liquor spill prevention and control programs have instituted a combination of these practices to substantially eliminate black liquor losses. It has been reported that the practical maximum reduction in BOD_5 raw wastewater loading that can be attained from spill prevention is 5 kg/kkg (23). Based upon site visits by the Agency, it appears that sulfite mills are less likely than kraft or soda mills to have engineered controls for collecting spills and leaks of pulping liquors at the immediate process areas.

Details of the practices listed above, and the associated estimated costs and effluent reduction benefits for mills that chemically pulp wood or other fibers are in the document entitled, "Technical Support Document for Best Management Practices for Spent Pulping Liquor Management, Spill Prevention, and Control" (24).

7.2.9 Maximizing Recovery Boiler Capacity

At kraft mills, spent cooking liquor (black liquor) from the digester and from brown stock washing is sent to the chemical recovery area, where it is concentrated in multiple-effect evaporators and then burned as part of the chemical recovery process. Section 4.2.4 in the TDD describes this process in detail. The organic fraction of the concentrated black liquor solids generates heat (captured as steam generated in the boiler) as it is burned, and the inorganic material produces a molten smelt in the hearth that is dissolved to regenerate the cooking chemicals.

When a mill improves its brown stock washing or installs oxygen delignification or extended cooking, it is common practice to recycle the resulting filtrates to the recovery boiler, thus increasing the amount of organics sent to the recovery boiler. The heating value of these

additional organics is an important factor in determining whether a mill needs to increase the burning capacity of its recovery boiler when it makes these process changes.

The increase in the heating load on the recovery boiler (referred to in this section as an increase in boiler capacity) depends not only upon the amount of organics coming from the process, but also upon their heating value. The heating value of the organics differs depending upon the wood (hardwood or softwood) and the process from which the organics are obtained. For example, the solids recycled from an oxygen delignification process have been oxidized and therefore have a lower heating value than those solids recycled from a brown stock washer or digester. Also, more organics are recovered from softwood pulp than from hardwood pulp.

In U.S. mills, the increase in recovery boiler capacity that results from improving brown stock washing alone is minimal (generally less than 1 percent) because, as indicated in Section 7.2.4, U.S. mills, on average, have fairly good brown stock washing. This contribution to the recovery boiler is negligible when the accuracy of boiler flow measurements is taken into account. However, the impact of extended delignification processes such as extended cooking and oxygen delignification is an important consideration in determining increases in recovery boiler capacity.

EPA prepared a detailed analysis of the impacts of extended cooking, oxygen delignification, screen room closure, improved brown stock washing, and other components of BAT and BMP on the kraft recovery system. This analysis is presented in the Analysis of Impacts of BAT Options on the Kraft Recovery Cycle (21). The main conclusion is that heat load on the boiler, not black liquor solids (BLS), is the key parameter determining boiler capacity. EPA's BAT cost model was adjusted to account for the impacts on the recovery system of additional black liquor recovered.

EPA estimated that the increase in thermal load from Option A will average 1.5 percent, with a maximum of 5 percent. For Option B, the average increase in thermal load is 2.2 percent, with a maximum of 8.7 percent. In estimating mill-specific costs, if the increase in thermal load to the boiler was estimated to be less than 1 percent, EPA provided no capital costs, assuming that this increase in load could be accommodated by improving boiler operation. For thermal load increases exceeding 1 percent, three options were available: the addition of anthraquinone, implementation of oxygen-based black liquor oxidation, and boiler upgrades (air system upgrades, improving liquor delivery, and firing high concentration black liquor, among others). Boiler upgrades are high-cost modifications that typically increase boiler capacity by 10 percent, and thus are not appropriate for accommodating the smaller thermal load increases EPA estimated would result from BAT. The TDD (Section 8.2.9) also discussed several other methods of increasing recovery boiler capacity.

Anthraquinone and oxygen-based black liquor oxidation are not recovery boiler modifications; they are means of reducing the thermal load on the boiler that can be employed even if a mill is recovery-boiler-limited. Anthraquinone is a catalyst that increases pulp yield and thus decreases the quantity of BLS to be burned for a fixed quantity of production.

Anthraquinone is only an option for reducing the thermal load on the boiler for mills not already adding it to the digester. Oxygen-based black liquor oxidation is not a common practice in the United States, but equipment for this process is sold by two major industrial gas vendors. In this process, black liquor is partially oxidized before it is fired to the recovery boiler, reducing the thermal load of the black liquor by about 5 percent. This technology could be applied only to mills with non-direct contact evaporator recovery boilers (because most direct contact evaporation recovery boilers are already equipped with black liquor oxidation to reduce odor emissions).

Because of concerns about which boilers at bleached papergrade kraft mills can accommodate the increase in thermal load that will result from BAT, NCASI surveyed the industry in 1995. NCASI provided the results of this survey to EPA. A recovery boiler has a margin of capacity to accommodate an increased black liquor load unless all possible modifications to a boiler have been made. Of 190 boilers represented in the survey, 78 (41 percent) show evidence of being operated at their maximum capacity. Even for these boilers, however, the reductions in thermal load provided by anthraquinone or oxygen-based black liquor oxidation can accommodate the small increased loadings from BAT and BMP.

While estimating the costs of BAT, EPA used the status of each boiler reported in the 1995 survey to determine if an adjustment to recover boiler capacity was required. For the 84 bleached kraft and soda mills for which compliance costs were estimated, EPA estimated the following recovery boiler capacity adjustments would be required:

	Option A (Number of mills requiring recovery boiler capacity adjustment)	Option B (Number of mills requiring recovery boiler capacity adjustment)
None	61	57
Anthraquinone	9	10
Oxygen Black Liquor Oxidation	13	16
Recovery Boiler Air System Upgrade	1	1

Thus, EPA concluded that most mills would not require adjustments to the thermal load to the recovery boiler (or upgrades to the boiler) to accommodate the increase in black liquor thermal load to the boiler that will result from BAT. No mills require recovery boiler rebuilds or replacements.

7.3 Pollution Prevention Controls Used in the Bleach Plant

This section describes applicable technologies for reducing and preventing pollutant discharges from bleach plants at chemical pulp mills. For most facilities, the Agency defines the bleach plant as including the stage where bleaching agents (e.g., chlorine, chlorine dioxide, ozone, sodium or calcium hypochlorite, peroxide) are first applied, each subsequent extraction stage, and each subsequent stage where bleaching agents are applied to the pulp. A limited number of mills produce specialty grades of pulp using hydrolysis or extraction stages prior to the first application of bleaching agents. For those mills, EPA considers the bleach plant to include those pulp pretreatment stages. Although oxygen delignification systems are integrated with pulping and chemical recovery systems, the convention in the industry is to include oxygen delignification when specifying bleach sequences (e.g., O D/C E_{op} D). The Agency is using that convention in this document, although it considers oxygen delignification to be part of pulping (prebleaching) rather than bleaching. Section 4.2.6.1 of the TDD presents an overview of bleach plant operation.

7.3.1 Ozone Bleaching

Ozone, a powerful oxidizer, has been studied for over 20 years as a potential replacement for chlorine and chlorine dioxide in the first stage of pulp bleaching. Historically, two major drawbacks have inhibited the adoption of industrial-scale ozone bleaching: high cost and poor selectivity (i.e., a high degree of carbohydrate degradation and therefore viscosity drop) (25). Recent technological developments, such as the introduction of medium-consistency ozone bleaching and improvements in ozone efficiency and selectivity, have removed these disadvantages to using ozone (25,26). Ozone bleaching technology continues to evolve. The first full-scale ozone bleaching systems in a sulfite mill and a kraft mill started up in 1991 and 1992, respectively.

Ozone is generated either from oxygen or air, though it is normally produced using oxygen. The oxygen (O_2) passes through a series of tubes and a high voltage is applied, causing the oxygen molecules to dissociate. The dissociated molecules recombine to form ozone (O_3) , which is relatively unstable. Since ozone can easily decompose back to oxygen, ozone must be generated on site for immediate use in the bleach plant.

Ozone bleaching has been researched at low, medium, and high consistencies. No full-scale low-consistency systems are in existence at this time. Most currently operating full-scale systems process the pulp at medium consistency (10 to 15 percent). Medium-consistency systems have lower capital costs than high-consistency systems do (26).

Oxygen delignification with effective post-oxygen washing is necessary prior to ozone bleaching to lower the lignin content of the pulp and therefore reduce the ozone charge required. No "target" kappa numbers are currently defined for the pulp entering the ozone stage; for ozone bleaching, target kappa numbers tend to be site-specific. Ozone oxidizes the carbohydrates in pulp as well as the lignin, so the ozone charge must be optimized to achieve the

maximum pulp delignification while minimizing the effects on pulp viscosity. Mills currently operating ozone bleaching systems use between 5 and 12 kg ozone per kkg of pulp, although actual application rates and operating conditions for this technology are usually confidential. A high-consistency system allows a higher ozone application rate than a medium-consistency system.

The processes and equipment used for ozone bleaching and oxygen delignification are similar. Prior to being fed to the ozone bleaching tower, the pulp is treated with either acetic or sulfuric acid to lower the pH. As with oxygen delignification, the pulp may be fluffed in the reactor to facilitate a more uniform reaction. Ozone is delivered to the reactor with an oxygen carrier gas. This carrier gas can be recovered after ozone bleaching, cleaned, and recycled to the ozone generator, or used elsewhere in the mill (e.g., in an oxygen delignification system or an oxygen-enhanced extraction stage).

The reaction of the pulp with the ozone normally takes a few minutes, as opposed to a few hours with other bleaching agents. The ozone bleaching reactor is therefore much smaller than other reaction vessels in traditional bleach plants.

Process effluents from ozone bleaching can be recycled to the recovery boiler, which decreases the volume of bleach plant effluent and the amount of non-chlorinated compounds discharged from the bleach plant. Because chlorine and chlorine derivatives are not used for first stage bleaching, chlorinated organic compounds (e.g., CDDs/CDFs, chlorinated phenolics) are not formed. The increase in the load of solids on the recovery boiler from recycling the ozone stage filtrate is lower than the increase from an oxygen delignification stage. The increase in solids for the ozone and subsequent extraction stages cause an additional heating load on the recovery boiler of approximately 1 percent (27).

In September 1992, a U.S. kraft mill began to produce lower brightness kraft pulp using ozone bleaching. This mill pulps and bleaches softwood to approximately 82-83 ISO; however, the bleaching sequence at this mill (OZED) includes a final chlorine dioxide brightening stage. The following description of this mill is based upon a recent publication (28).

This mill reports significant environmental benefits from the OZED bleaching sequence compared to sequences CEDED and OD/CED for both hardwood and softwood for parameters such as color, BOD₅, COD, chloroform, and AOX. Although chlorine dioxide is used in the final bleaching stage, 2,3,7,8-TCDD has not been detected in D-stage filtrate or bleached pulp. Another advantage of this sequence is the potential to recycle filtrates from the oxygen, ozone, and extraction stages to the recovery system. Compared to bleaching sequences of CEDED and OD/CED, the OZED sequence achieves equivalent pulp properties, except for viscosity, for both hardwood and softwood. Since pulp viscosity and strength have a different correlation for oxygen/ozone bleached pulps than for chlorine compound bleached pulps, the mill reports that the decrease in viscosity has not been a problem.

Additional environmental benefits and further recycling of filtrates could be achieved if the final chlorine dioxide stage were to be converted to use a non-chlorine containing compound. The mill has studied combinations of oxygen and ozone with peroxide and believes that an acceptable softwood TCF pulp can be made. The mill does not currently use a TCF bleaching sequence because it would substantially increase operating costs over the cost of the OZED sequence.

7.3.2 Improved Mixing and Process Control

To realize the full benefits of technologies such as high chlorine dioxide substitution, oxygen-enhanced extraction, and oxygen delignification on the bleach plant effluent, the pulp and bleaching agents must be well mixed and the chemical addition rate controlled as precisely as possible. Normally, when these technologies are installed, mixing and process control are also upgraded.

High shear mixers, introduced in the late 1970s, dramatically increased the contact of the pulp with gases such as oxygen, making the oxygen-enhanced extraction stage a practical, effective bleaching technology (29). High shear mixing has similarly become a vital part of a medium-consistency oxygen delignification system. To ensure uniform application of the chemicals in a high chlorine dioxide substitution stage, the pulp must be well-mixed with the chlorine dioxide. EPA has included costs for high shear mixers at individual mills as necessary.

7.3.3 Chlorine Dioxide Substitution

In the late 1980s and early 1990s, bleached kraft mills began substituting chlorine dioxide (ClO₂) for some or all of the molecular chlorine normally used in the first bleaching stage. This process became known as chlorine dioxide substitution, and became common practice in the industry at that time because ClO₂ substitution reduces the formation of chlorinated organics in the bleach plant effluent and lowers bleach plant chemical consumption (4).

As mills used more and more ClO₂, additional benefits were realized such as further reductions in chlorinated organics in bleach plant effluent and more consistent and improved pulp quality because it minimizes cellulose degradation. Then mills began to use complete (100 percent) substitution of ClO₂ for chlorine. By mid-1995, over 32 percent of bleached kraft production in the United States was made using complete ClO₂ substitution, and many companies had committed to installing the technology on additional bleach plants. By 1996, 67 percent of bleached kraft production in Canada was made using complete ClO₂ substitution (30).

The amount of ClO₂ used is expressed as percent substitution and is defined as the percentage of the total chlorine bleaching power of the first bleaching stage that is provided by chlorine dioxide. It is calculated by the following formula:

Percent Substitution =
$$\frac{2.63 \text{ (ClO}_2 \text{ in kg/kkg)}}{2.63 \text{ (ClO}_2 \text{ in kg/kkg)} + \text{ (Cl}_2 \text{ in kg/kkg)}}$$
(1)

where 2.63 equals the oxidizing power of chlorine dioxide compared to chlorine. Chlorine dioxide is a stronger oxidizing agent than chlorine. Consequently, less chemical is required when chlorine dioxide is substituted for chlorine.

Chlorine dioxide must be generated on site because it is unstable and cannot be transported in a pure form by truck or rail. As of January 1, 1993, most mills that bleach chemically pulped wood pulps generated chlorine dioxide on site, and more than 60 percent of those mills used chlorine dioxide substitution in the first bleaching stage, as shown below:

Subcategory	Total Number of Mills	Number With ClO ₂ Generation On Site	Number With ClO ₂ Substitution in First Bleaching Stage
Bleached Papergrade Kraft and Soda	87	79	60
Papergrade Sulfite	10	5	4

In generating chlorine dioxide, byproducts are produced. Sodium sulfate (Na_2SO_4) and chlorine are generated in different amounts, depending on the chlorine dioxide generator, as shown below (31):

Chlorine Dioxide Generator	Cl ₂ (kkg/kkg ClO ₂)	Na ₂ SO ₄ (kkg/kkg ClO ₂)	
Solvay	0	3.5	
Mathieson	0	3.5	
R2	0.66	7	
R3	0.66	2.4	
R8	0	1.4	

It is important to control the ratio of chlorine applied in the first bleaching stage to lignin content of the pulp entering the first bleaching stage, as well as the amount of ClO_2 substitution, to most effectively reduce the formation of chlorinated compounds (4). The ratio of total chlorine (from molecular chlorine and chlorine dioxide) in the first bleaching stage

(expressed as percent on pulp) to kappa number of the pulp entering the first bleaching stage is referred to as the active chlorine multiple (ACM) or kappa factor:

Kappa Factor (ACM) =
$$\frac{[\text{Cl}_2 \text{ (kg/100 kg brown stock)} + 2.63 \text{ ClO}_2 \text{ (kg/100 kg brown stock)}]}{\text{Pre-chlorination kappa number}}$$
(2)

A Canadian study evaluated the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF in the final effluent from bleached kraft mills relative to ClO₂ substitution and ACM (29). The study developed an equation for the relationship between ClO₂ substitution and ACM which is described in Section 8.3.5 of the TDD. For complete ClO₂ substitution, the study equation predicts that TCDDs and TCDFs will not be formed if an ACM of 0.48 or less is used. The detection limits in the study were 10 ppq for 2,3,7,8-TCDD and 30 ppq for 2,3,7,8-TCDF.

EPA's data, described in a separate document (32), show that 2,3,7,8-TCDD is normally not detected at mills using complete ClO₂ substitution but that 2,3,7,8-TCDF is occasionally detected below 30 ppq (even when the ACM is below 0.48). This document also shows that the 12 chlorinated phenolic compounds regulated by this rule are normally not detected at mills using complete ClO₂ substitution and that chloroform generation is substantially reduced for these mills compared to conventional bleaching sequences.

7.3.4 Enhanced Extraction

In the alkaline extraction stages of the bleach plant, lignin reaction products from the preceding acid stages are dissolved, or extracted, by applying sodium hydroxide (caustic) solutions to the pulp. These dissolved products are then washed from the pulp. The first caustic extraction stage of the bleach plant can be enhanced with oxygen, hydrogen peroxide, or both (shown as E_o , E_p , and E_{op} , respectively) to replace equivalent quantities of chlorine-based bleaching chemicals in other bleaching stages (34). Enhanced extraction is a low capital cost measure that improves effluent quality by reducing chlorine consumption, therefore reducing the amount of chlorinated organics in the bleach plant effluent. Mills implementing enhanced extraction typically reduce molecular chlorine use in the first bleaching stage, while keeping the chlorine dioxide addition rate constant (resulting in a higher level of chlorine dioxide substitution).

Oxygen-enhanced extraction became commercially feasible in the early 1980s due to the development and introduction of high shear mixers for pulp stock. A high shear mixer is required to ensure good mixing of the gaseous oxygen with the pulp. The extraction must be carried out in either an upflow extraction tower or a downflow tower preceded by a small upflow pre-retention tube to maintain the pressure required to keep the oxygen gas in solution until it has reacted with the pulp. Adding oxygen to the extraction stage improves delignification by approximately 25 percent (35), while allowing the mill to use less chlorine or chlorine dioxide in the overall bleaching sequence. Adding between 4 and 6 kg of oxygen per kkg of pulp saves approximately 2 kg of active chlorine per kg of oxygen (29).

Oxygen-enhanced extraction normally reduces overall bleaching chemical costs, thus justifying, in many cases, the capital cost of the additional mixing power and piping required. Data from many mills in the U.S. that converted their bleaching sequences from E to $E_{\rm o}$ operation during the 1980s support this fact.

Hydrogen peroxide is usually added at the inlet to the oxygen mixer when E_{op} is used, or at the inlet to the stock pump for E_p alone. Adding hydrogen peroxide in the first extraction stage improves delignification and reduces chlorine-based chemical requirements either in the first chlorination stage or further along in the bleaching sequence. Applying 1 kg of peroxide per kkg of pulp results in an active chlorine savings of approximately 2 to 3 kg (31). If hydrogen peroxide-enhanced extraction is used following 100 percent chlorine dioxide substitution, a higher final brightness can be achieved (29).

Mills that use hydrogen peroxide-enhanced extraction are able to reduce the amount of either molecular chlorine or chlorine dioxide in other bleaching stages. The cost of hydrogen peroxide is currently much higher than the cost of molecular chlorine and slightly lower than the cost of chlorine dioxide (see Section 10). Therefore, a mill operating hydrogen peroxide enhancement increases its operating costs if it reduces molecular chlorine use, but decreases operating costs if it reduces chlorine dioxide use.

Adding oxygen to an extraction stage is more capital intensive than adding peroxide because, as described above, a high shear mixer and other equipment must be used for the bleaching stage to operate effectively. Therefore, the simplest way for a mill to enhance its extraction stage is with hydrogen peroxide. Unlike oxygen, hydrogen peroxide is also effective in enhancing the second extraction stage. In addition, the bleaching power of the Eop stage can be increased by raising the temperature, which is another strategy to reduce bleaching chemical charge at relatively low cost.

A significant number of U.S. bleached pulp mills have implemented enhanced extraction. As of January 1, 1993 and mid-1995, the number of mills using some form of enhanced extraction were:

Subcategory	Total Number of Mills	Number With Enhanced Extraction in 1993 $(E_o, E_p, \text{ or } E_{op})$	Number With Enhanced Extraction in 1995 $(E_o, E_p, \text{ or } E_{op})$
Bleached Papergrade Kraft and Soda	87	65	77
Papergrade Sulfite	10	4	6

7.3.5 Elimination of Hypochlorite

Sodium hypochlorite and calcium hypochlorite are effective bleaching agents that attack lignin. Sulfite pulps are more easily bleached with hypochlorite than kraft pulps because the lignin is more easily solubilized (19). Hypochlorite can also degrade cellulose, decreasing pulp viscosity. To limit cellulose degradation, hypochlorite is usually applied in an intermediate bleaching stage for kraft pulps.

Chloroform is generated when pulp is bleached with hypochlorite (36). Mills that use sodium or calcium hypochlorite in one or more bleaching stages generate approximately ten times as much chloroform as mills using a CEDED bleaching sequence (37). Controlling chloroform releases generally entails eliminating hypochlorite as a bleaching agent. The bleaching power of hypochlorite can be replaced by chlorine, chlorine dioxide, peroxide, and/or oxygen. However, replacing hypochlorite with chlorine is counterproductive if the purpose is to reduce chloroform generation, because bleaching with molecular chlorine also generates chloroform.

For some mills, particularly mills with short bleaching sequences (e.g., CEH), eliminating hypochlorite requires replacing the hypochlorite bleaching tower with a new chlorine dioxide tower, washer, and auxiliaries made of materials resistant to the more corrosive environment of chlorine dioxide bleaching. Some mills may be able to modify the bleaching chemical additions to other stages (i.e., adding oxygen and/or peroxide to the first extraction stage) and abandon the hypochlorite stage, rather than replacing it. Mills with a CEHDED-type of bleaching sequence and mills that use hypochlorite only in extraction stages may be able to eliminate the hypochlorite stage.

Replacing hypochlorite reduces direct operating costs, because hypochlorite is more expensive than chlorine dioxide, oxygen, and peroxide. Hypochlorite also has a lower chlorine equivalence factor (see Section 10). The number of mills using a hypochlorite stage or hypochlorite-reinforced extraction as of January 1, 1993 and mid-1995 are shown below:

Subcategory	Total Number of Mills	Mills Using Hypochlorite in 1993	Mills Using Hypochlorite in 1995
Bleached Papergrade Kraft and Soda	87	36	20
Papergrade Sulfite	10	9	7

7.3.6 Strategies to Minimize Kappa Factor and DBD and DBF Precursors

As noted in Section 7.3.3 in this document, the control of the kappa factor (or ACM) in the first bleaching stage is an important process control parameter. EPA's data and the data of other researchers indicate that particular chlorinated organic pollutants are not detected in bleach plant effluent when bleaching kappa factors are maintained below certain values. In

particular, Shariff el al. (38) studied TCDF and, for ClO₂ bleaching, developed the following relationship:

TCDF ~ (precursor concentration) (kappa factor)⁴

Assuming this relationship is correct, to minimize the formation of TCDD/F, process operators should minimize:

- 1. Kappa factor; and
- 2. Precursors contained in the pulp entering the bleach plant.

Each strategy is discussed separately below. This discussion also appears in EPA's Comment Response Document (39). Some of the strategies for minimizing kappa factor are discussed in more detail in separate subsections of this section but are briefly repeated here for completeness of this discussion.

Minimizing Kappa Factor

Strategies for minimizing kappa factor include:

Reducing first stage kappa factor and shifting bleaching to later stages that are not implicated in TCDD/F formation;

Optimizing conditions in the first bleaching stage for most efficient use of the ClO₂ applied;

Improving process control so that kappa factors are not permitted to fluctuate;

Modifying the extraction stages by peroxide and/or oxygen reinforcement and operating at a higher temperature;

Reducing knots, compression wood, dirt, and shives by improving screening or operating oxygen delignification; and

Reducing black liquor carryover by improving pulp washing.

Each of these strategies is discussed below.

Shifting bleaching to later stages - Bleaching is a multi-stage process in which, historically, acid chlorine bleaching stages are alternated with alkaline extraction stages. This multi-stage process provides considerable flexibility to mill operators in terms of where they make the bleaching reactions happen. Mills producing high brightness pulp generally have five bleaching stages ($D_0ED_1ED_2$). They can reduce the kappa factor in the D_0 stage and increase the

bleaching power of later stages by reinforcing the extraction stages with oxygen and peroxide and if necessary, increasing the ClO_2 charge in the D_1 and D_2 stages.

Optimizing first stage bleaching conditions - Reeve (40) reports that ClO₂ required to reach a target kappa number (CEK) is a function of pH, chloride ion concentration, the type of pulp, and extraction stage conditions. If pH is too high, for example, required kappa factor will increase. Georgia-Pacific reported that control of first stage pH was key to effective low kappa factor bleaching (41). Insufficient chloride ion concentration will also increase the required kappa factor. Pulp mill bleaching conditions such as pulp consistency, temperature, retention time, and pulp cleanliness are extremely varied. In addition, the objective of bleaching, in terms of target brightness, cleanliness and strength differ among products and mills. Because of this variety, bleaching conditions must be optimized for each product produced at each mill.

Improving process control - At some mills, the quality of unbleached pulp entering the first stage of bleaching is poor and inconsistent. The kappa number may vary widely over space and time. If a constant bleaching chemical application rate is used, the kappa factor also varies widely. To control kappa factor thus means controlling the kappa number. Extended cooking and oxygen delignification produce pulps with a more uniform and constant kappa number than the pulp produced by many conventional pulping operations. Improved mixing also produces a more uniform pulp. In addition, in-line kappa number measuring instruments with feed-back controls are used to adjust the chemical application rate to the measured kappa number. A charge of bleaching chemical can also be applied stepwise to improve process control (42).

Peroxide and oxygen reinforced extraction - It has become common practice to compensate for a lower kappa factor by using peroxide and/or oxygen in the second stage $(E_p \text{ or } E_{op})$. This strategy can also reduce operating costs, because peroxide is less expensive than chlorine dioxide. In addition, the bleaching power of the E_{op} stage can be increased by raising the temperature, which will reduce the required kappa factor at relatively low cost.¹

Reducing dirt and shives entering the bleach plant - Conventionally pulped wood contains dirt (colored particulate matter) and shives (intact fiber bundles). Dirt and shives can be removed by bleaching. Often, the ClO₂ charge is established to meet dirt specifications, and may exceed the charge necessary to meet brightness specifications. Improved chip size control (to remove knots and compression wood for improved pulping), improved brown stock screening, oxygen delignification, and extended cooking reduce dirt and shives entering the bleach plant making possible the use of lower bleaching chemical charge (a lower kappa factor).

¹In addition to reducing the potential for the formation of TCDD/F, reduced kappa factor minimizes bleaching costs. Reeve and Dence (1996) report that after balancing the ClO₂ applied in the first stage with the ClO₂, peroxide, and oxygen used in later stages, the most cost effective kappa factor is 0.14 to 0.16, depending on wood species.

Reducing black liquor carry-over by improving pulp washing - Poorly washed pulp carries a large quantity of black liquor into the bleach plant. Black liquor contains the non-fibrous fraction of raw wood that is separated from the fiber during pulping, as well as the spent cooking chemicals. This black liquor carry-over consumes oxidizing (bleaching) chemicals. For a poorly washed pulp, a higher kappa factor is required to achieve the same degree of delignification in the first bleaching stage than is required for a well-washed pulp.

Minimizing Precursors

The results reported by EPA and Shariff et al. indicated that TCDF can still be formed at mills that have eliminated obvious sources of DBD and DBF precursors such as contaminated defoamers and kerosene. Thus, some TCDF precursors must be contained in brown stock pulp. This pulp is a mixture of cellulose fiber, lignin, and black liquor carry-over. Hise (43) and Hrutfiord (44) have speculated that precursors could originate from lignin fragments that accumulate in the black liquor after pulping.

Berry (45) found that precursor concentration can be decreased by steam stripping brown stock pulp to remove volatile components. Berry (46) explains that steam stripping is an inherent part of high consistency oxygen delignification and also occurs when brown stock pulp is released from the digester at a temperature at which steam is driven from the pulp. Berry (45) found that processing pulp through an oxygen delignification stage using nitrogen-gas instead of oxygen removed precursors. Because no oxidation occurred under these test conditions, Berry concluded that the precursor removal was a result of the physical actions of the washing and steam stripping. Others conclude that oxygen delignification will oxidize a significant portion of the lignin monomers (47), again, resulting in reduced precursor levels.

Hrutfiord (44) found that greater quantities of TCDD/F are formed in the chlorination of compression wood than normal wood. Compression wood, prevalent in knots, is the main source of *p*-hydroxyphenyl which can form DBD and DBF.

Pulping digester and evaporator condensates, derived from black liquor, contain many of the same constituents as the black liquor itself. The condensates are frequently treated to remove foul-smelling TRS and then to wash pulp prior to bleaching. It has been hypothesized that inadequately treated condensates used to wash oxygen delignified pulp are a source of TCDD/F precursors (Francis, Personal Communication, 1992).

Removal of TCDD/F precursors, including lignin monomers² contained in black liquor, could be accomplished through:

²If the TCDF precursors are actually in the lignin, a relationship should exist between kappa number into bleaching and TCDF. Data collected by EPA and data submitted by Shariff et al. do not demonstrate this conclusion, possibly because kappa factor has a much more significant impact on the formation of TCDF than precursor concentration.

Brown stock washing that achieves extremely low carry-over of organic compounds;

Oxygen delignification (through increased washing, steam stripping, or other physical mechanisms or, possibly, by chemical oxidation of precursors);

Removal of knots (compression wood) from brown stock pulp prior to bleaching; and

Use of only precursor-free pulping and evaporator condensates in post-oxygen delignification washing.

7.3.7 Enzyme Bleaching

Enzymes are organic compounds that act as catalysts in reactions. Xylanase enzymes improve the bleachability of wood pulps by partially hydrolyzing the xylan (the primary bonding agent between the cellulose and the lignin) although the exact mechanism by which they aid in bleaching is not known (48). The lignin is therefore more easily removed in subsequent bleaching stages. Xylanase may be added to the pulp after brown stock washing or after oxygen delignification to reduce or eliminate the need for bleaching with chlorine compounds. The optimum conditions for the xylanase reaction are temperatures between 40 and 55 between 4 and 6, and retention time between 0.5 and 3 hours (48). The xylanase is applied at less than 1 kg/kkg of pulp.

Several mills worldwide have conducted full-scale trials with xylanase on kraft pulps with resulting increases in brightness and viscosity and no loss of pulp strength (48). More experimental work has been done using enzymes to bleach kraft pulps than to bleach sulfite pulps.

7.3.8 Peroxide Bleaching

Though hydrogen peroxide is primarily used to reinforce caustic extraction stages, hydrogen peroxide can replace chlorine compounds in bleaching chemical pulps. The brightness achievable using peroxide can be increased by lowering the lignin content of the pulp as much as possible prior to bleaching (e.g., by using oxygen delignification).

While bleaching stages that use chlorine compounds inherently remove metal ions (e.g., Ca, Mg, Na, etc.) from the pulp, these ions will react with peroxide to form hydroxyl radicals that can degrade cellulose. Therefore, the metal ions must be removed from solution by using chelating agents, followed by effective pulp washing prior to applying peroxide (49). When a peroxide stage follows a chlorine compound bleaching stage, separate addition of a chelating agent is not required. One method of peroxide bleaching using chelating agents is the Lignox® process developed by Eka Nobel (50).

The peroxide charge required for a full peroxide stage is approximately 2.5 percent on pulp. To fully use the peroxide charge and achieve high brightness requires a temperature of between 70 and 90 decrease pulp viscosity (49).

Peroxide bleaching has been demonstrated in full-scale applications at both kraft and sulfite mills outside the U.S. The capital cost of implementing peroxide bleaching is minimal, assuming use of existing bleaching towers. Because the unit cost for hydrogen peroxide is higher than for chlorine, operating costs for peroxide bleaching may be higher depending upon the amount of peroxide used. The cost of the large amount of peroxide that is necessary to bleach a pulp to full brightness has limited the use of peroxide bleaching.

7.3.9 Totally Chlorine-Free Bleaching of Papergrade Kraft Pulps

Totally chlorine-free bleaching is performed without the use of chlorine, sodium or calcium hypochlorite, chlorine dioxide, chlorine monoxide, or any other chlorine-containing compound. TCF bleaching is performed using a combination of enzymes, ozone, oxygen, and/or peroxide. In the last several years, numerous TCF bleaching processes have been developed and are now used at bleached papergrade kraft mills worldwide.

Section 8.3.11 of the TDD reported briefly the status of TCF bleaching at papergrade kraft mills in 1993. At that time about 15 mills worldwide were making some TCF bleached pulp but few of the mills were dedicated to TCF production due to a lack of market demand. Also, most of the TCF pulps were bleached to a lower brightness than market kraft grades (75-80 ISO vs 88-90 ISO). Therefore, EPA concluded that TCF was not an available pollution prevention technology because of limited worldwide experience with this process and a lack of data for TCF bleaching of softwood to full market brightness.

EPA received many comments that it should continue to investigate TCF bleaching because dioxin and furan are not generated at any level with TCF bleaching, thus assuring that these pollutants are not released to the environment. The Agency conducted two sampling programs at the one U.S. mill that produces softwood TCF bleached kraft pulp. EPA collected samples of bleach plant filtrates but could not collect samples of treated effluent because the mill does not employ secondary treatment. The Agency also conducted a sampling program at a Nordic mill that produces hardwood and softwood kraft pulp on two bleach lines that alternate between elemental chlorine-free (ECF) and TCF bleaching. Samples collected at this mill could not be used to characterize treated TCF bleaching effluents, because the TCF bleaching effluents are combined with ECF bleaching effluents for treatment.

Both of the sampled softwood TCF fiber lines employed oxygen delignification followed by multiple stages of peroxide bleaching. The U.S. mill's unbleached pulp kappa number was between 7 to 10. The bleach sequence for the U.S. mill is $QE_{op}PPPS$ (51). Q represents an acidic chelant stage, followed by an enhanced extraction stage (E_{op}) , three alkaline peroxide stages (PPP), and the addition of sodium bisulfite (S). Bleached pulp brightness was

approximately 79 during the first sampling episode at the U.S. mill, but by the time of the second sampling episode pulp brightness had increased to 83 ISO. The Nordic mill uses extended cooking, and was able to reduce the lignin content of unbleached pulp to a low kappa number of four. The Nordic mill bleach sequence is QPPP. At the time of sampling, this mill bleached pulp to a brightness of 83 ISO.

At neither mill was chloroform or chlorinated phenolic pollutants detected in samples collected by EPA. At the U.S. mill, dioxin, furan, and AOX were not detected above the analytical minimum level during sampling fully representative of TCF operations. The average bleach plant AOX loading measured by EPA at the Nordic mill was 0.002 kg/ADMT (compared to a long-term average of 0.51 kg/ADMT for Option A). EPA's dioxin sampling results for the Nordic mill were surprising. Dioxin was detected at a concentration just above the minimum level in one sample of combined bleach plant filtrate, when the mill was bleaching without the use of chlorine or any chlorinated compounds. Furan was not detected. EPA believes the dioxin results were unique to the operation of this mill and does not conclude that TCF bleaching generates dioxin.

Neither of the two sampled mills produced softwood pulp at full market brightness. By the end of 1996, two mills were producing exclusively TCF pulp that was fully bright and fully strong (see Section 8.7.2 of this document). Data in EPA's record are insufficient to confirm that TCF bleaching processes are technically demonstrated for the full range of products made with bleached kraft pulp. Despite these impediments, EPA believes that the progress being made in TCF process development is substantial, and that additional data may demonstrate that TCF processes are indeed available for the full range of market products. TCF mills will qualify for at least Tier I of the Voluntary Advanced Technology Incentives Program.

7.3.10 Totally Chlorine-Free Bleaching of Papergrade Sulfite Pulps

Section 8.3.14 of the TDD reported briefly the status of TCF bleaching at papergrade sulfite mills in 1993. At that time at least 10 mills worldwide were making TCF bleached sulfite pulp. EPA visited one of these mills to collect bleach plant effluent samples. As of 1995, two U.S. sulfite mills were using TCF bleaching processes.

The bleaching sequences at most of the TCF papergrade sulfite mills are based on oxygen delignification, followed by one or more peroxide bleaching stages. Many of these mills describe their oxygen delignification stage as an enhanced extraction stage (E_{op}); however, in form and function it is the same as oxygen delignification (i.e., a pressurized tower is used to introduce oxygen to lower the pulp lignin content). Further delignification, or bleaching, is performed with one or more peroxide stages. The peroxide stages are operated at consistencies ranging from 12 to 30 percent; peroxide charges vary between 30 and 40 kg/ADMT. To prevent side reactions of metal ions in the peroxide stages, some mills use acid washes or add chelating agents before, between, or in the peroxide stages. Some mills also add sodium silicate or nitrilamine to peroxide stages to further brighten the pulp.

The furnish used by papergrade sulfite mills using TCF bleaching include a variety of hardwoods (predominately birch and beech) and softwoods (mostly spruce). These TCF sulfite mills also make a variety of products including market pulp, tissue, and printing and writing grades. Bleached pulp properties vary by product. Most mills report brightnesses near 85 ISO; the range reported is 70 to 90 ISO.

7.4 <u>End-of-Pipe Wastewater Treatment Technologies</u>

This section describes the BAT component of efficient biological treatment. More detailed information about the wastewater treatment processes in use at pulp and paper mills is presented in Section 8.5 of the TDD.

According to EPA's 1990 Census Questionnaire, more than 80 percent of direct discharging pulp and paper mills in the United States use primary and secondary (biological) wastewater treatment, while only 2 percent use tertiary treatment. Indirect discharging mills discharge to POTWs, which also use secondary wastewater treatment.

Primary treatment is the removal of suspended solids. Primary treatment may also include other pre-biological treatment processes such as equalization, neutralization, or cooling. Secondary treatment involves a biological process to remove organic matter through biochemical oxidation. In the pulp and paper industry, activated sludge systems and aerated/non-aerated basin systems are the most commonly used biological processes. Tertiary treatment is advanced treatment, beyond secondary, to remove particular contaminants. Examples of tertiary treatment are the removal of phosphorus by alum precipitation and removal of toxic refractory organic compounds by activated carbon adsorption.

Common elements of wastewater treatment, as practiced in the pulp and paper industry, include (but are not limited to):

are not limited to):
Primary sedimentation;
Neutralization;
Equalization;
Precooling;
Nutrient addition;
Aeration;
Multi-basin systems, some of which act as polishing ponds;
Mixed or hybrid treatment systems (activated sludge and basin systems operated in series or parallel); and

Addition of flocculants to secondary clarifiers to improve settling.

As noted in Section 8.5 of the TDD, the operation of treatment systems is important to achieving optimum effluent quality, particularly the activated sludge systems which require careful day-to-day attention to numerous important operating parameters. EPA defined efficient biological treatment as that which removes 90 percent or more of the influent BOD₅. Most papergrade kraft and sulfite mills are achieving 90 percent BOD₅ removal (see TDD Table 9-8 based on data from the 1990 Census Questionnaire data). NCASI also reported greater than 90 percent BOD₅ removals for direct discharging mills and for POTWs receiving chemical pulp mill wastewater.

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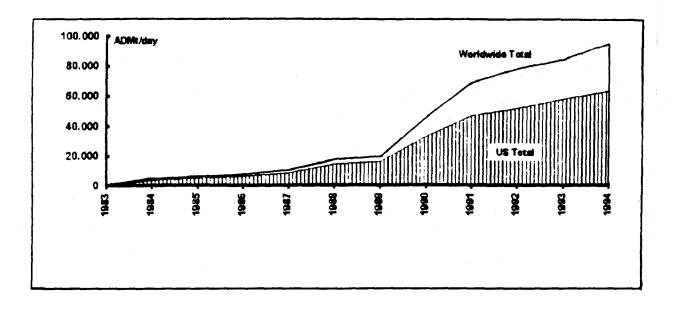


Figure 7-1. U.S. and Worldwide Increase in Kraft Pulp Produced by Extended Cooking, 1983-1992

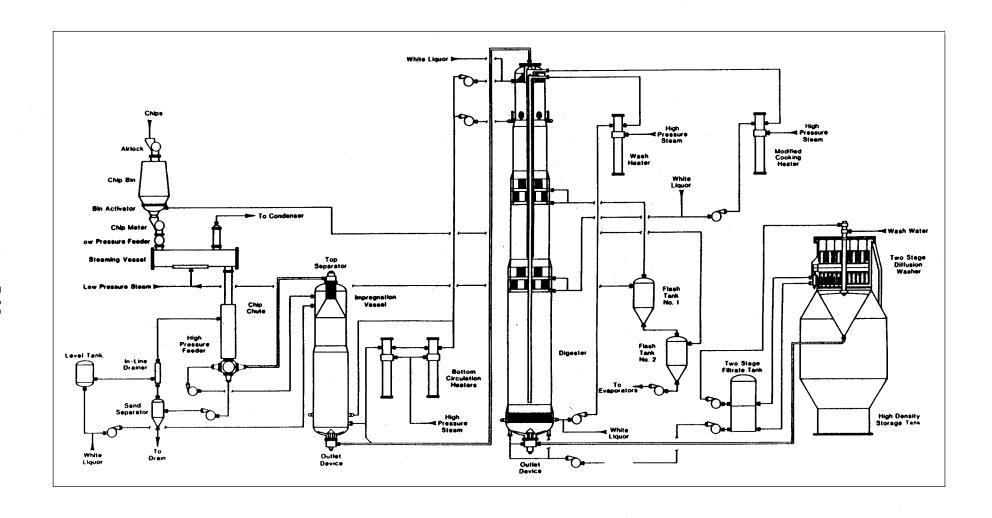


Figure 7-2. Extended Cooking Continuous Digester System (EMCC®)

Courtesy of Kamyr, Inc., Glens Falls, New York.

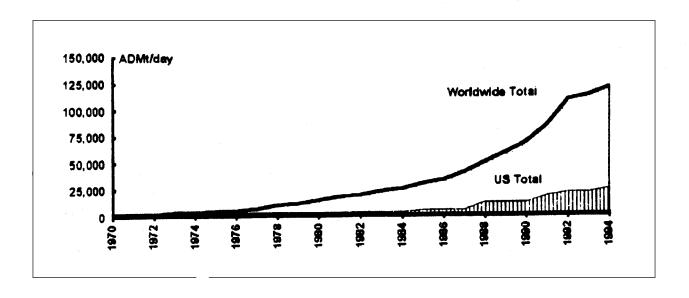


Figure 7-3. U.S. and Worldwide Increase in Kraft Pulp Produced by Oxygen Delignification, 1970-1992

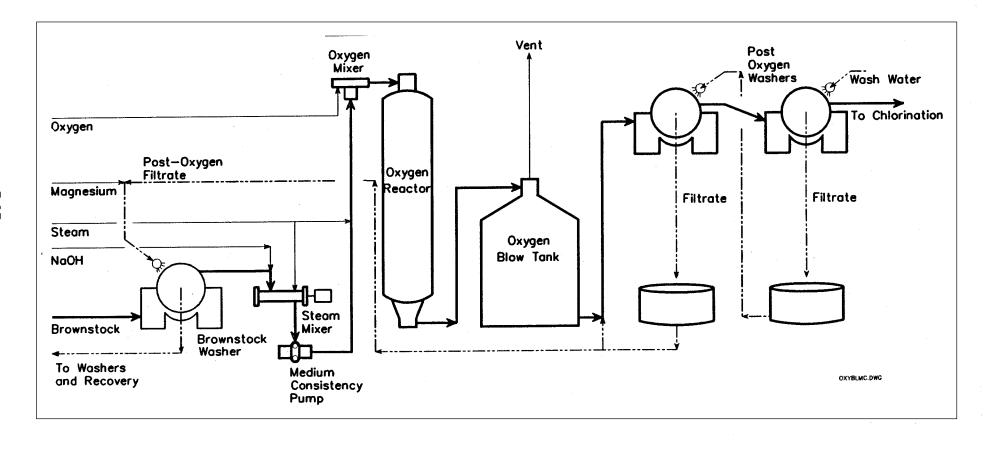


Figure 7-4. Typical Medium-Consistency Oxygen Delignification System

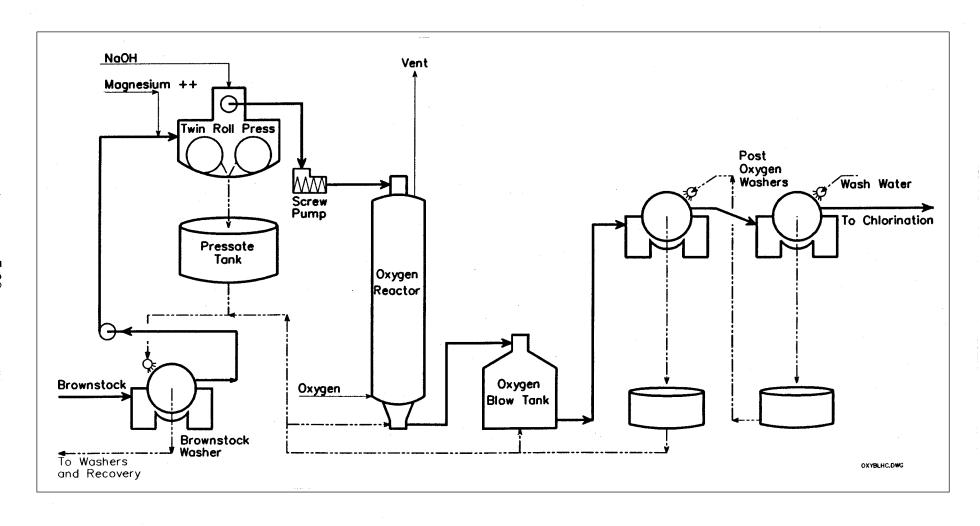


Figure 7-5. Typical High-Consistency Oxygen Delignification System

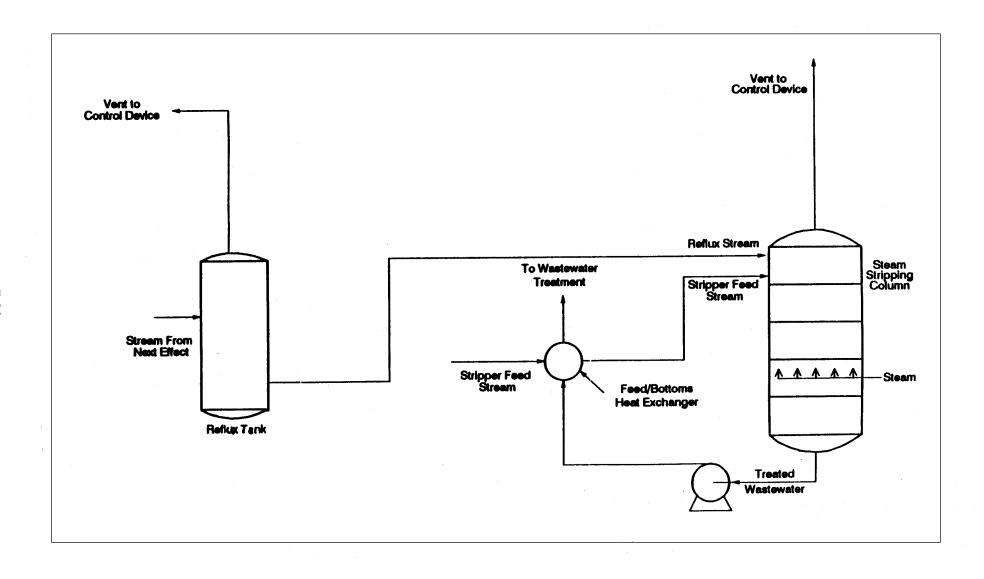


Figure 7-6. Continuous Steam Stripper System